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CHEMICAL CHARACTERIZATION OF MODEL AEROSOLS

Warren Schwartz, et al

Battelle Columbus Laboratories

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A variety of polyfunctional reaction products were identified, including alcohols, aldehydes, ketones, carboxylic acids, and phenols. Tentative identification of nitrogen containing products was also accomplished, including nitrate esters and aromatic nitro compounds.

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Air Pollution	Aerosol Chemistry	07-E
Chemical Analysis	Atmospheric Chemistry	
Gas Chromatography	Organic Chemical Analysis	
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CHEMICAL CHARACTERIZATION OF MODEL AEROSOLS

by

Warren Schwartz

Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

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EPA Project Officer: Ronald Patterson

Chemistry and Physics Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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ABSTRACT

Model aerosols were generated from individual hydrocarbon precursors and nitrogen oxides under simulated atmospheric conditions in a 17.3 m^3 environmental chamber. Hydrocarbon precursors employed were toluene, alpha-pinene, and cyclohexene. Aerosols were collected on glass-fiber filters and organic matter was obtained by solvent extraction. Organic reaction products were fractionated into acid, neutral, and basic components, and were analyzed in detail by techniques including gas chromatography and gas chromatography combined with mass spectrometry. The study also included evaluation of techniques for selective derivatization of aerosol products.

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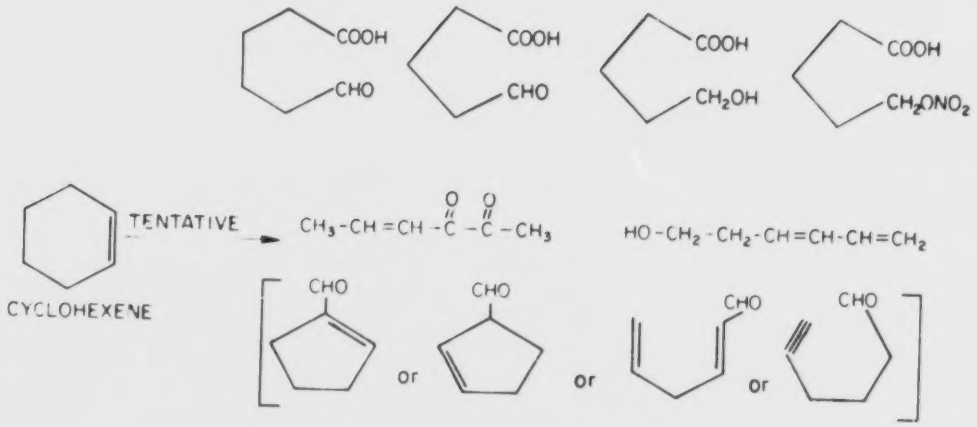
SECTION I

SUMMARY AND CONCLUSIONS

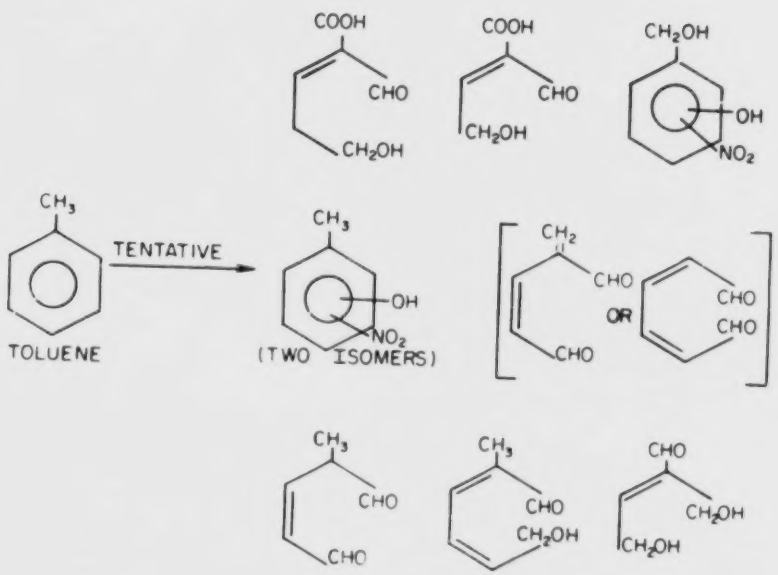
This study has been directed toward detailed organic chemical characterization of aerosols generated from individual hydrocarbon precursors under simulated atmospheric conditions. Model aerosols were generated using the Battelle-Columbus Laboratories' 17.3 m^3 environmental chamber. Systems studied during this program include cyclohexene/NO_x, toluene/NO_x, and α-pinene/NO_x. Aerosol was collected on glass-fiber filters and organic matter was obtained by sequential solvent extraction. Reaction products were fractionated into acid, neutral, and basic components and were analyzed in detail by techniques including gas chromatography and gas chromatography combined with mass spectrometry (GC-MS). Additionally, techniques were evaluated for the selective derivatization of aerosol products. This was directed at "tagging" specific functional groups with easily detectable markers. Overall, the objective of the analytical effort was the identification of individual reaction products formed from each hydrocarbon precursor. By comparing the structure of such products with the parent hydrocarbon, and with each other, we may infer the types of organic reactions occurring under atmospheric conditions.

Tentative identification of a variety of aerosol products has been accomplished. The results of this study are best summarized by reference to these products. In considering the structures shown below it should be emphasized that these are tentative identifications.

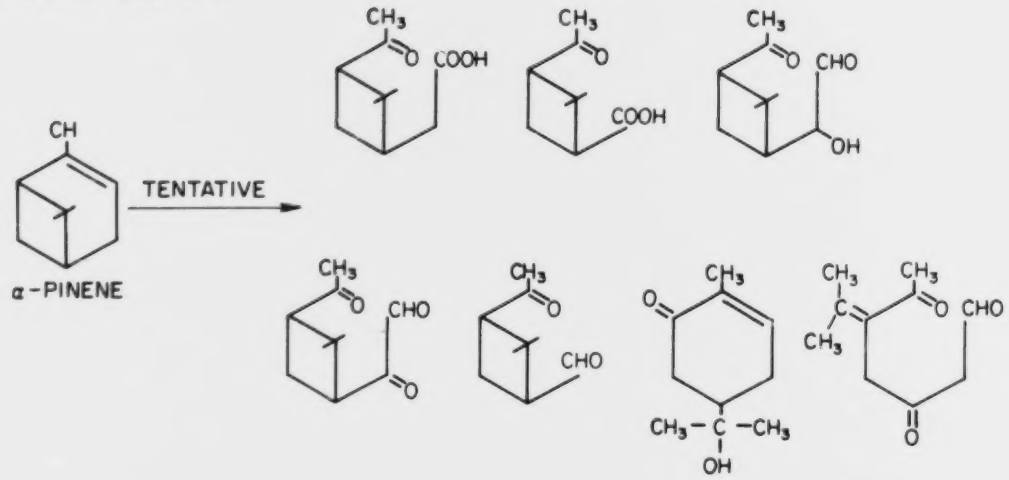
Cyclohexene aerosol.



Toluene aerosol.



α-Pinene aerosol.



In view of the reaction conditions, formation of many of the above aerosol products is not particularly surprising. Oxidative cleavage of carbon-carbon double bonds is to be expected in an ozone containing atmosphere. Oxidative decarboxylation and formation of alcohols, carboxylic acids and carbonyl compounds is consistent with free radical processes expected in the atmosphere. Nevertheless, experimental demonstration of the formation of such products should be of value.

The fate of nitrogen oxides in the atmosphere has long been a question of interest. In this context, the current research has included identification of two classes of nitrogen-containing products. Nitrate esters were tentatively identified in cyclohexene aerosol, and aromatic nitro compounds were tentatively identified in toluene aerosol. This infers that nitration of an aromatic ring is occurring under atmospheric simulation. Identification of such nitrate esters and nitropenols is of interest from the standpoints of both fundamental atmospheric chemistry and health effects.

In studying model aerosols, it is often possible to characterize reaction products more easily than if these products were present in the more complex mixture of atmospheric organics. Moreover, identification of interesting compound types in model aerosol suggests that such compounds may be present in atmospheric aerosol. For example, during earlier phases of this research* the formation of 5-nitratopentanoic acid was reported. Subsequently, such nitrate esters were identified in atmospheric aerosol during elegent mass spectral studies of Schuetzle, Crittenden, Cronn, and Charleson[1]** Thus, characterization of model aerosols is complementary to and supportive of research directed toward characterization of atmospheric aerosol.

An ultimate objective of model aerosol research is the development of a comprehensive basis for predicting the types of products that can be expected to form when specified organic compounds are released into the atmosphere. Needless to say, this objective remains quite distant. It is hoped that the results of this study have contributed to the attainment of that goal.

*See Background and Introduction section.
**References are listed on page 125.

SECTION II

BACKGROUND AND INTRODUCTION

It is by now well established that the aerosols which form as a result of photochemical smog reactions are composed predominantly of organic matter. Because of the complexity of smog formation little is known of the pathways by which organic vapors undergo chemical change to become aerosols. The ultimate objective of this research program is the elucidation of organic chemical reactions involved in such aerosol formation. An understanding of these processes would allow us to predict the types of aerosol products that would be formed from a particular pollutant. Moreover, a comprehensive understanding of such reactions might allow us to assign sources contributing to the atmospheric hydrocarbon burden.

Analysis of atmospheric particulate matter reveals a complex mixture of organic components. Similarly, the organic vapors emitted into the atmosphere, the compounds that fuel photochemical aerosol formation, also represent a highly complex mixture. It is not surprising, therefore, that it has been difficult, if not impossible, to correlate observed components of atmospheric particulate with specific organic pollutants or well-defined organic reactions. In view of this complexity, this research has been based on the study of simple and controllable model aerosol systems.

Many model studies have examined the factors influencing aerosol formation, and the time course of this phenomenon. These studies[2-27] have considered such parameters as NO_x concentration, SO_2 concentration, relative humidity, and stirring of reactants within the chamber. The aerosol-forming tendency

of various hydrocarbons has similarly been evaluated.[28,29] Research concerned with the mechanism of aerosol formation has involved electron microscopic examination of aerosol particles[30,31].

In contrast to such studies, the research reported herein has been directed toward characterization of specific aerosol reaction products formed from individual hydrocarbons. Few studies have involved detailed characterization of this type.[1,32-34] A notable exception is the model aerosol research conducted during the first year of the program "Haze Formation--Its Nature and Origin"[34]*. This program sponsored jointly by the Environmental Protection Agency (CPA 70-Neg 172) and the Coordinating Research Council (CAPA 6-68) was the direct predecessor of the current study. For the sake of clarity and completeness, salient aspects of that study are included in this report.

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*Research concerning composition of model aerosols conducted during the "Haze Formation" study was supported in part by Grant AP-00828 from the Office of Research Grants, EPA. The principal investigator was William E. Wilson.

SECTION III

RATIONALE AND METHODS OF PROCEDURE

Despite the reduced complexity of model aerosols compared to atmospheric aerosol, the reaction mixtures generated during atmospheric simulation are indeed complex. Thus, the analytical scheme employed was designed to reduce this complexity and simplify characterization of individual reaction products.

During the first year of this study, emphasis has been placed on characterization of aerosol products that have not undergone extensive oxidation or degradation. Identification of such compounds is profitable in that the products characterized can be more easily related to the parent hydrocarbon. On the basis of this relationship we may infer the types of reactions occurring under atmospheric simulation. The extraction and fractionation procedures described below were designed to separate the reaction mixture into defined components with varying degrees of oxidation/degradation. Detailed analyses were conducted using the less degraded fractions of the reaction mixture.

It is recognized that many interesting and significant products may be present in the more highly oxidized fractions. Indeed, such products are more abundant than the less degraded components. Although the first year's study has emphasized characterization of the less oxidized reaction components, future work will include analysis of the more highly oxidized materials.

Under the headings below, further rationale concerning the experimental approach is discussed, and methods of procedure are described.

SELECTION OF HYDROCARBON PRECURSORS

Toluene, α-pinene, and cyclohexene were selected as precursors for the generation of model aerosols. Selection was based on a number of criteria. First, it was desired to include hydrocarbons of various classes, and where feasible, to select members of these classes which represent important contributors to the atmospheric hydrocarbon burden. Also taken into account was the aerosol reactivity of candidate hydrocarbons[35]. Hydrocarbons having high aerosol reactivity were favored in view of the need to obtain sufficient aerosol mass for analysis. All hydrocarbons studied to date in this program are active aerosol formers. Future work will include compounds of more limited reactivity, such as branched alkanes.

Inspection of early morning hydrocarbon distribution data in both East[36] and West[37] Coast cities indicates that aromatic hydrocarbons comprise between 30 and 40 percent of the nonmethane hydrocarbon. Of these, toluene is the most abundant, comprising approximately 25-40 percent of the total aromatics. Study of this compound permits us to observe the behavior of both an aromatic ring, and an alkyl substituent under conditions of atmospheric simulation.

It has been reported that approximately 175 million tons of reactive hydrocarbons are released into the atmosphere annually from tree foliage sources[38,39]. This is over sixfold greater than the estimated 27 million tons released from technological sources. The major compounds released by plants and trees are the monoterpenes (C_{10}), and the semiterpene isoprene (C_5). It has been speculated that the natural "blue haze" observed in many forested regions arises from the atmospheric reactions of these compounds. α-Pinene, chosen for use in this study, is one of the principal monoterpenes emitted from these sources[38,39]

Selection of cyclohexene was made on a somewhat broader basis. The above-cited studies of early morning hydrocarbon distribution in East and West Coast cities indicates that olefins comprise between 10 and 20 percent of the total nonmethane hydrocarbon. Olefins having four or more carbon atoms comprise about 25 percent of the total olefin fraction. Smog chamber studies[35] have demonstrated that such olefins have considerable propensity to form organic aerosols, the aerosol-forming tendency increasing with the molecular weight of the olefin. Although cyclohexene is rarely detected in urban atmospheres, this compound is known to be a particularly prolific aerosol precursor. This stems in part from the fact that cleavage of the cyclohexene double bond leads to formation of bifunctional oxidation products. Compared to monofunctional products formed from acyclic olefins, these bifunctional products have decreased volatility and greater tendency to enter the aerosol phase. In view of the desireability of obtaining high aerosol mass loadings, cyclohexene was selected for study.

GENERATION OF MODEL AEROSOLS

Model aerosols were generated using the Battelle-Columbus 17.3 m^3 environmental chamber. In selecting the conditions for aerosol generation, it was necessary to strike a compromise between the desire to operate at the relatively low reactant concentrations typically observed in authentic atmosphere, and the need to provide sufficient aerosol mass for organic analysis. Typically, ~10 ppm (vol/vol) hydrocarbon was used. Nitrogen oxide concentrations ranging from 2-5 ppm ($NO + NO_2$) were employed, and were selected and adjusted to obtain reaction kinetics typical of photochemical smog manifestations. Preliminary runs were conducted to determine suitable reactant concentrations for each aerosol system studied.

The reactant concentrations employed are at least an order of magnitude greater than atmospheric levels. The effect of the higher reactant concentrations on the aerosol chemistry is uncertain. In general, however, most of the chemical reactions responsible for smog formation are first order in reactants, and the first encounter an intermediate has with another potentially reactive species is nearly always with oxygen molecules. Therefore, only in instances where the overall speed of radical-radical reactions approaches that of radical-O_2 reactions will the overall reaction pathways of intermediates be seriously affected by the higher concentration of reactants. Judging from the small fraction of reactions meeting this condition, it is believed that the concentrations employed did not result in a serious departure from normal smog chemistry. This argument, of course, is oversimplified; however, until a detailed understanding of aerosol reaction mechanisms is developed further, speculation on the importance of concentration in these simulations is unwarranted.

Smog Chamber Characteristics

The smog chamber utilized in these studies is approximately 2.4 m high, 4.9 m long, and 1.5 m wide, having a volume of approximately 17.3 m^3. The surface-to-volume ratio is 0.78. The inside surface consists of 35.3 m^2 of polished aluminum and 9.2 m^2 of FEP-Teflon windows (5 mil thick) through which the reaction mixture is irradiated using an external bank of lamps. The lamp bank consists of 96 fluorescent "black" lamps and 15 fluorescent sunlamps. The spectral distribution of the black lamps peaks in intensity at 370 nm; the sunlamps peak intensity occurs at 310 nm. Light intensity generated corresponds to a k_d of 0.45 min^{-1} as determined by NO_2 photolysis and o-nitrobenzaldehyde actinometry. This intensity is comparable to that of noonday sun over the wavelength integral of NO_2 absorption.

Air supplied to the chamber is taken in through a 10-m stack atop a three-story building, and is passed through a purification system including a permanganate filter bed, a charcoal filter system, an absolute filter, and a humidification unit. After purification, background total-hydrocarbon is generally 1-3 ppmC with the majority of this being methane. A trace of background ethane is occasionally, observed by gas chromatography. Olefins and aromatics have always been below gas chromatographic detection limits. Sulfur dioxide is always below the detection limit of a flame photometric detection (~10 ppb) and carbon monoxide background levels are generally between 1 and 3 ppm as measured by nondispersive infrared spectroscopy. Light scattering readings are essentially the same as for clean air (Raleigh scattering) and the condensation nuclei count is generally less than 200 particles per cubic centimeter.

Smog-Chamber Cleanup

Prior to each series of experiments with a different model hydrocarbon, it was necessary to thoroughly clean the chamber's surface to prevent cross contamination of aerosol products. Such cross contamination had been observed during previous studies[34]. Cleanup was accomplished by washing down chamber surfaces with a spray of 4:1 isopropanol:water. Prewashed cloths were used to scrub the surfaces and surgical scrub suits were worn to prevent contamination from street clothing. Throughout the procedure, the chamber was maintained on purge (8500 l min^{-1}). Nevertheless, the high concentration of solvent vapor that develops, requires that the chamber be sealed and that the worker be provided with an auxiliary breathing apparatus.

After cleanup, the chamber was purged overnight and was then permitted to stand with 1 ppm ozone for several hours. Before generation of aerosol for analytical use, a "conditioning" run was conducted using the model system to be studied.

Aerosol Generation, Monitoring, and Collection

Detailed data concerning reactant concentrations and conditions are shown in Table 1 (p. 25). After initial concentrations were established, the mixing fan was turned off and irradiation was begun. Parameters monitored throughout the course of the experiment included NO and NO_2 concentration using a continuous Saltzman analyzer, total hydrocarbon concentration using a flame ionization detector, ozone concentration using a chemiluminescence analyzer, and light scattering using an integrating nepheloneter.

In general, irradiation was continued until light scattering measurements indicated that maximum aerosol growth had occurred. After this maximum was observed, irradiation was halted and the aerosol was collected by evacuating the chamber contents through tared 10-cm-diameter glass-fiber filters (Gelman Type A) using a high-volume type sampler. Typically, about 11 m^2 of chamber volume was sampled over a 30-minute period. Before use, the filters were washed repeatedly, first with distilled-in-glass methanol, and then with methylene chloride. They were then equilibrated at 50 percent R.H. and tared. After collection, the filters were reequilibrated, weighed, and placed in glass containers for storage at -60 C. After a series of runs was completed, collected aerosol was subjected to Soxhlet extraction, as described below.

EXTRACTION OF AEROSOL PRODUCTS

Collected aerosol was subjected to Soxhlet extraction first with methylene chloride, and then with either acetone or methanol. The sequential extraction procedure was used in order to obtain reaction products having a wide range of oxidation state and polarity. The methylene chloride extracts are expected to contain products less oxidized than those obtained in the methanol or acetone extracts.

Thus, consistent with previously discussed rationale, the methylene chloride extractable matter was used for subsequent detailed analysis. Extraction with the more polar solvent was conducted in order to provide a measure of weight-percent extractable into solvents of varying polarity, and to obtain the more oxidized reaction products for possible analysis during future work. Values for weight-percent extractable (see Results and Discussion section) should be valuable in that they permit comparisons of data for model aerosols with that obtained for atmospheric aerosol.

It should be emphasized that samples were collected on prewashed filters. Soxhlet extraction of such prewashed filters was conducted, and blank values for weight-percent extractable were determined.

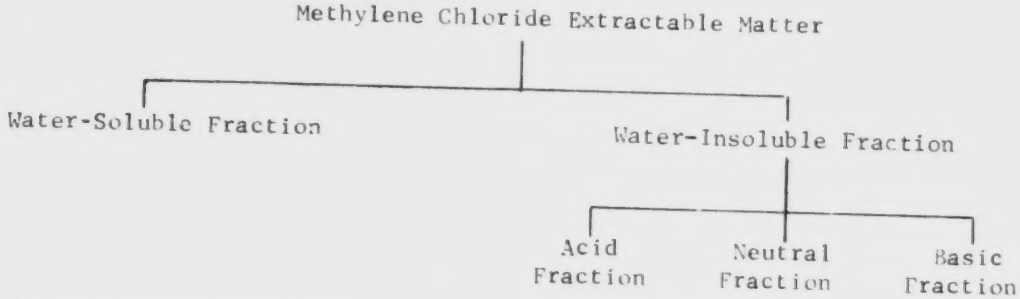
Extraction Procedures

All extractions were conducted using high-purity "distilled-in-glass" solvents (obtained from Burdick and Jackson, Muskegon, Michigan). Methylene chloride extractions were run for 20 hours; methanol or acetone extractions were run for 44 hours. Approximately 25 ml of solvent was used for each 10-cm-diameter filter disk. The volume of extract was reduced to 1-3 ml using a Kuderna-Danish fractionating column. In order to determine values for weight-percent extractable, a small aliquot (~1 percent) of the concentrated extract was taken to dryness on a light (~5 mg) aluminum weighing pan. Pans were tared and reweighed using a Cahn Electrobalance, and aliquot weights were determined to ± 2 μg. From these data the total weight of extractable matter was calculated. Values for weight-percent solvent extractable were calculated as shown below. In making these calculations a correction was made to account for filter blank.

$$\text{Weight-percent solvent extractable} = \frac{\text{(weight of extracted matter, corrected)}}{\text{(weight of total particulate)}} \times 100$$

FRACTIONATION OF AEROSOL EXTRACTS

As noted previously, detailed analyses were conducted using methylene chloride extractable matter. In order to simplify the analytical task, the extractable matter was fractionated according to the scheme below.



The water-insoluble fraction can be expected to contain the relatively less oxidized, less degraded components of the reaction mixture. In keeping with the previously expressed objective of this phase of the study, detailed analyses were conducted using the water-insoluble fraction. Further fractionation into acid, neutral, and basic components was performed in order that analyses could be conducted using mixtures partially defined according to chemical class. For example, in analyzing a neutral fraction, one might anticipate the presence of aldehydes, ketones, or alcohols, but not carboxylic acids or phenols.

Fractionation Procedures

The methylene chloride extractable matter was fractionated into water-soluble and water-insoluble components by extracting the methylene chloride solution (~3 ml) four times with 2 ml portions of distilled water. All extractions were conducted in conical centrifuge tubes agitated using a vortex mixer. This procedure permits convenient centrifugation of emulsions prior to separation of phases, and minimizes sample losses. Water was removed by lyopholization, and the weight of the water-soluble fraction was determined.

The water-insoluble material remaining in solution was next extracted four times with ~2-ml portions of 2N aqueous sodium hydroxide and twice with ~2-ml portions of distilled water. The sodium hydroxide and water washes were combined.

The methylene chloride solution was then extracted three times with ~2-ml portions of 2N hydrochloric acid and twice with ~2-ml portions of distilled water. The acid and water washes were combined. Additional water washes were made until neutral; these were discarded. Material remaining in methylene chloride solution after extraction with both aqueous sodium hydroxide and hydrochloric acid is defined as the water-insoluble neutral fraction.

The sodium hydroxide extract (containing organic-acid salts) was brought to pH ~0.1, and the free acid was extracted into methylene chloride using a continuous liquid/liquid extractor for 96 hours. Similarly, the hydrochloric acid extract (containing organic-base salts) was brought to pH ~13, and the free base was extracted into methylene chloride, again using a continuous liquid/liquid extractor for 96 hours. The methylene chloride solutions containing the acid,

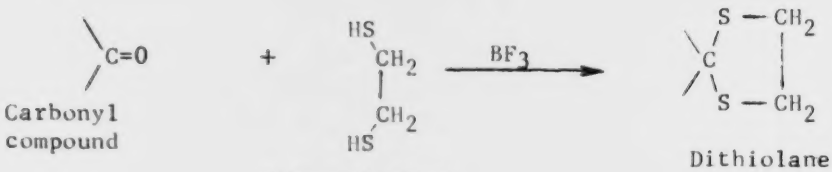
basic and neutral fractions were dried by refluxing the solutions over a 3-A molecular sieve. Drying the solutions directly with anhydrous magnesium sulfate or molecular sieve was found to be unsatisfactory because of irreversible adsorption of organics upon the drying agent.

The dried solutions were concentrated to a volume of ~1 ml using a Kuderna-Danish fractionating column. The weight of organic matter in the concentrated solutions was determined by taking an aliquot of the concentrate (~5 percent) and evaporating the solvent on a light (~5-mg) aluminum weighing pan. Pans were tared and reweighed using a Cahn Electrobalance, and aliquot weights were determined to ±2 μg. Using values determined for the weights of the various fractions, weight percent distribution values were calculated.

DERIVATIZATION OF AEROSOL PRODUCTS

In order to aid product characterization, the program included study of selective derivatization of aerosol reaction products. This was directed at "tagging" specified functional groups with easily detectable markers. This is useful in that the mass spectral data often do not permit unambiguous identification of the functional groups in a sample. It is especially true where gas chromatography combined with mass spectrometry is performed at unit resolution. In such casesthe empirical formula cannot always be determined with certainty. Thus, a study of selective derivatization was undertaken to assess the usefulness of this approach to aerosol characterization.

Specific derivatization of carbonyl groups and hydroxyl groups was investigated. Derivatization of carbonyl groups was conducted by reaction with ethanedithiol to form corresponding dithiolanes as shown in the reaction below.



Carbonyl compound

Ethanedithiol

Dithiolane derivative

Dithiolanes can be selectively detected using flame-photometric gas chromatography. Additionally, they produce distinctive fragmentation patterns upon mass spectrometric analysis.

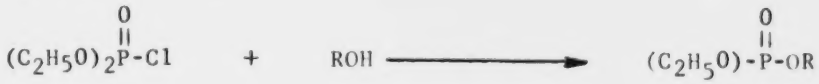
Various reagents for derivatization of hydroxyl groups were investigated, including

1. Trifluoroacetyl imidazole, $CF_3-\overset{O}{\overset{\|}{C}}-N$ (imidazole)
2. Heptafluorobutyryl imidazole, $C_3F_7-\overset{O}{\overset{\|}{C}}-N$ (imidazole)
3. Heptafluorobutyryl chloride, $C_3F_7-\overset{O}{\overset{\|}{C}}-Cl$
4. Pentafluorobenzoyl chloride, $C_6F_5-\overset{O}{\overset{\|}{C}}-Cl$
5. Diethylchlorophosphate, $(C_2H_5O)_2\overset{O}{\overset{\|}{P}}-Cl$.

The fluorinated acyl chloride and acyl imidazole reagents react with hydroxyl functions to form fluorinated ester derivatives. These can be selectively detected by electron-capture gas chromatography.

$$\text{or } \begin{matrix} R(F)-\overset{O}{\overset{\|}{C}}-Cl \\ R(F)-\overset{O}{\overset{\|}{C}}-IM \end{matrix} + ROH \longrightarrow R(F)-\overset{O}{\overset{\|}{C}}-OR$$

Diethylchlorophosphate reacts with hydroxyl groups to form the corresponding phosphate ester.



Such derivatives can be selectively detected by flame-photometric gas chromatography. Thus, the phosphates can be analyzed using the same instrument and detector as is used for analysis of the dithiolanes. Like dithiolanes, phosphates produce strikingly characteristic mass spectral fragmentation patterns.

Finally, it should be noted that, prior to the analysis of the acid fraction by gas chromatography and GC-MS, it was treated with diazomethane. This commonly used reagent converts carboxylic acids and phenols to relatively volatile methyl esters and methyl-aryl ethers, thereby permitting gas chromatographic analysis.

Preparation of Dithiolane Derivatives

The procedure employed for preparation of dithiolanes was adapted from methods reported by Fieser[40,41] and by Corey et al.[42] Typically, 1-10 mg of an authentic carbonyl compound or aerosol product was mixed with 0.5 ml of ethanedithiol and 0.5 ml of distilled BF_3-etherate in a 3-ml reaction vial with Teflon-lined screw-cap. The reaction mixture was heated at 60 C overnight. It was then cooled and diluted with 5-10 ml of "distilled-in-glass" methylene chloride. The methylene chloride solution was then washed twice with an equal volume of distilled water, three times with 10 percent aqueous sodium hydroxide, and again, twice with distilled water. Extractions were conducted in conical centrifuge tubes agitated using a vortex-mixer. This permits convenient centrifugation of emulsions prior to separation of phases.

After the above cleanup, the methylene chloride solution was dried by refluxing over molecular sieve (3A), and the dried solution was concentrated to a volume of 1 ml using a Kuderna-Danish fractionating column. The concentrate was retained for analysis by gas chromatography and GC-MS.

Preparation of Perfluoroester Derivatives

Preparation of perfluoroester derivatives of alcohols was conducted using reagents 1-4 above and was performed according to a procedure adapted from Pierce Chemical Company product literature[43]. Typically, 2 mg of authentic alcohol or aerosol product was mixed with 200 µl of dry pyridine in a 1-ml reaction vial with Teflon-lined screw cap. To this was added ~200 mg of acyl chloride or acyl imidazole reagent. Combination of reactants was conducted in a glove bag under dry nitrogen. The reaction mixture was then heated at 60 C for 2-6 hours.

Workup of the reaction mixture was begun by slowly adding 1 ml of ice cold distilled water to destroy excess reagent. The mixture was extracted three times with 2-ml portions of chilled "distilled-in-glass" hexane. Extractions were conducted in a conical centrifuge tube agitated using a vortex mixer. The hexane solution was dried, concentrated and retained for analysis by electron-capture gas chromatography.

Preparation of Phosphate Derivatives

The derivatization procedure was adapted from methods reported by Corey[44] and by Brown[45]. Typically, 2-20 mg of authentic alcohol or aerosol product was combined with 0.5 ml of dry 2,6-lutidine and 0.25 ml of diethylchlorophosphate in a 3-ml reaction vial with Teflon-lined cap. The vessel was closed securely and the mixture was heated to 60 C for 30 min, and was then permitted to stand at room temperature overnight.

Workup of the reaction mixture was begun by slowly adding 1 ml of distilled water to destroy excess reagent. The mixture was then washed into a conical centrifuge tube using ~5 ml of distilled-in-glass methylene chloride. The solution was extracted once with ~3 ml of distilled water, three times with 1N hydrochloric acid, once again with distilled water, three times with 1N aqueous sodium bicarbonate, and finally, twice with distilled water. All wash solutions were chilled in an ice bath before use, and extractions were conducted using a conical centrifuge tube agitated by means of a vortex mixer.

After workup, the methylene chloride solution was dried by refluxing over 3-A molecular sieve. It was then concentrated to 1 ml using a Kuderna-Danish fractionating column. The concentrate was retained for analysis by gas chromatography and GC-MS.

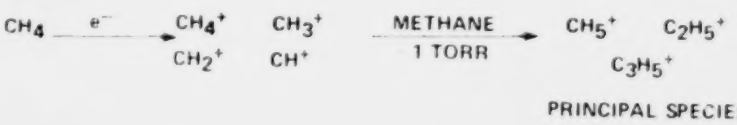
ANALYSIS OF AEROSOL PRODUCTS BY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

After extraction, fractionation, derivatization, and preliminary analysis by gas chromatography, the aerosol reaction products were analyzed by gas chromatography combined with mass spectrometry. Analyses were performed using a quadrupole mass spectrometer. The ion source of this instrument has been modified to permit generation of either chemical ionization or electron impact mass spectra. Most of the analyses conducted during this study were performed in the chemical ionization mode.

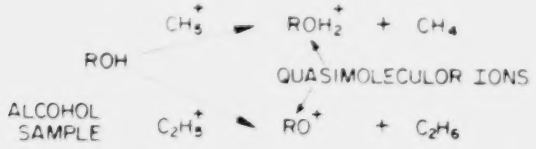
During the last several years there has been a marked increase in use of chemical ionization mass spectrometry. Nevertheless, it is probably less familiar to many analytical chemists than conventional electron impact spectrometry. Since a considerable number of chemical ionization spectra are presented in this report, some of the basic

characteristics of the technique are reviewed briefly below.

In chemical-ionization spectrometry, the sample molecules are ionized by means of vapor state interaction with ions of a "reactant gas". The reactant gas most commonly used is methane. As shown in the reaction sequence below, the methane is ionized by electron impact causing formation of a series of primary ions. At pressures of about 1 torr, these react further with methane to produce the secondary ions shown. These secondary ions are the principal species present in the ion source of the spectrometer



The secondary ions cause ionization of the sample molecules by donating a proton or abstracting a hydride ion. As shown in the reactions below, this interaction leads to formation of quasimolecular ions having mass/charge (m/e) one unit greater than or one unit less than the molecular weight (M) of the sample molecule. The quasimolecular ions are almost always observed; generally they are prominant.



There is also a tendency for the sample molecule to form an adduct with the $C_2H_5^+$ ion or the $C_3H_5^+$ ion. When this occurs "satellite ions" are observed at m/e values corresponding to M + 29 and M + 41. The observation of the quasimolecular ion and satellite ions facilitates the assignment of molecular weight. During this study use of GC-MS has thus permitted tentative assignment of molecular weights for the majority of principal chromatographic peaks in a sample.

In general, chemical ionization mass spectra show a great deal less fragmentation than electron impact spectra. In addition, the fragment ions that are observed generally arise from elimination of functional groups as small neutral molecules. Thus, chemical ionization spectra are often easier to correlate with structural features than are electron impact spectra.

In some cases chemical ionization spectra were obtained using helium as the reagent gas. Helium ions are species of much higher energy than the secondary ions of methane. The resulting spectra show far more fragmentation than those obtained using methane. The helium spectra are, in fact, very similar to classical electron-impact spectra. Generation of both methane and helium chemical-ionization spectra often aids in characterizing the sample.

Finally, it should be emphasized that the mass spectral characterizations presented in this report are almost invariably referred to as "tentative". Firm identifications can only be made when reference spectra are available for comparison. In view of the relatively recent advent of chemical-ionization mass spectrometry extensive compilations of such reference spectra are unavailable. Thus in many instances authentic compounds were obtained, and reference spectra determined in attempts to confirm tentative assignments.

This approach was used extensively during analysis of the α-pinene aerosol.

The interpreted spectra shown in the report include varying numbers of significant peaks which have not been rationalized. Many such peaks arise from the presence of contaminating compounds which elute simultaneously with the assigned product. In analysis of complex mixtures by GC-MS many spectra will show such contributions from multiple components.

Gas Chromatographic and Mass Spectral Procedures

Gas chromatographic separations were performed using a 3-m x 2-mm-ID (1/4-in-OD) Pyrex column packed with 3 percent OV-17 on Gas Chrom Q. Typically, analyses were performed with temperature programming, 100 - 250 C at 4 C/min. Two dual detector chromatographs were used in the study, a Varian Model 1700 equipped with flame-photometric detector and flame-ionization detector, and a Varian Model 2100 equipped with electron-capture detector and flame-ionization detector.

Analysis by GC-MS was performed using a Finnigan 1015 Mass Spectrometer. Instrument control and data acquisition were accomplished using a System Industries 150 data acquisition system. The reconstructed gas chromatograms shown in this report were computer generated. The detector response in these chromatograms was derived from the total ion current observed during successive scans on the spectrometer. Typically in this study, scans were repeated every 8 seconds. Thus, the x-axis of a reconstructed gas chromatogram is roughly equivalent to retention time. Desired spectra are recalled from computer memory (disk) by reference to the spectrum number.

SECTION IV

RESULTS AND DISCUSSION

SMOG CHAMBER IRRADIATIONS

Irradiation conditions and smog manifestations characterizing the model aerosols are shown in Table 1. The values listed represent averages for the respective hydrocarbon series. There was very little run-to-run variation in the parameters; the magnitude of such variation was insufficient to be of any consequence to the composite aerosol composition.

In general, the smog reactions in both the cyclohexene and α-pinene series were very fast as evidenced by the rapid rate of NO photooxidation (Table 1, $NO_{t1/2}$ values). The NO photooxidation rate in the toluene series was considerably less in spite of the higher HC/NO_x ratio employed. These trends in relative hydrocarbon reactivity toward NO photooxidation are similar to those reported in the literature.(35)

EXTRACTION OF AEROSOL PRODUCTS

Collected aerosol was subjected to sequential solvent extraction. Cyclohexene aerosol was extracted first using methylene chloride and then acetone. Toluene and α-pinene aerosols were extracted first using methylene chloride and then methanol. Values for weight-percent solvent extractable are shown in Table 2.

As noted previously, collections were made using prewashed glass fiber filters. In calculating values shown in the table, filter background (blank) has been subtracted. Soxhlet extraction of prewashed filters gave blank values of 0.007 mg per 10-cm-diameter disk for methylene chloride extraction and 0.27 mg per 10-cm-diameter disk for methanol extraction.

It is interesting to compare values shown in the table with those of weight-percent extractable observed for atmospheric particulate matter,

TABLE I. SUMMARY OF IRRADIATION CONDITIONS AND SMOG PARAMETERS[a]

	Hydrocarbon		
	Cyclohexane	Toluene	2-Pinene
Number of runs	2[b]	2	1
Irradiation period, min	180	270	120
Relative humidity			
Initial, percent	65	61	62
Final, percent	50	47	54
Hydrocarbon			
Mass irradiated, g	0.809	0.49	1.422
Initial concentration, ppm C	61	71	106
Final concentration, ppm C[c]	20	40	36
Nitric oxide			
Initial concentration, ppm	2.4	1.8	2.0
$t_{1/2}$, min[d]	15	75	22
Nitrogen dioxide			
Initial concentration, ppm	2.4	1.2	2.0
Maximum concentration, ppm	4.8	1.4	4.0
Ozone			
Maximum concentration, ppm	0.46	0.3	0.086
t_{max}, min	180	14	35
Light scattering[e]			
Maximum, 10^{-4} m^{-1}	110	180	220
Mass loading[f], mg m^{-3}	11.0	1.4	33
Percent conversion[g]	28.0	2.8	40
Total aerosol mass collected,[h] g	0.190	0.125	1.341

[a] Data shown are averages for the series of runs, except for values of total aerosol mass collected, which represent the total mass collected during an entire series of runs.

[b] After conditioning, a series of four cyclohexane runs was conducted. Aerosol from two of the runs was compromised during work-up.

[c] Includes contribution from product formation.

[d] Time at which one half the initial amount of NO was oxidized to NO_2.

[e] Indicates values are outside the normal operating range of the integrating nephelometer.

[f] Mass loading was calculated by dividing the aerosol mass collected by the effective volume sampled. The effective volume sampled was calculated by measuring the decrease in total organic carbon during the sampling period and multiplying this fractional decrease by the chamber volume.

[g] Percent conversion was calculated as total aerosol mass per mass of hydrocarbon irradiated. Total aerosol mass was calculated from the indicated mass loading multiplied by the chamber volume of 17.1 m^3.

Table 2. SOLVENT EXTRACTION OF COLLECTED AEROSOL

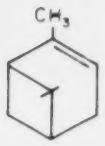
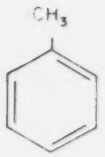
Hydrocarbon	Total Aerosol Mass Extracted, g	First Extraction, Weight-Percent Methylene Chloride Extractable	Second Extraction		Total Extractable Matter, Weight-Percent
			Solvent	Weight-Percent Solvent Extractable	
Cyclohexene	0.390	62	Acetone	31	93
Toluene	0.125	46	Methanol	43	89
α-Pinene	1.341	92	Methanol	1	93

such as those reported in the second annual report on "Haze Formation -- Its Nature and Origin"[46]. During that study, atmospheric particulate matter was collected in Columbus, Ohio, New York City, and Pomona California. It was similarly subjected to solvent extraction first using methylene chloride, and then dioxane. (Dioxane was used as the polar solvent in order to minimize extraction of the considerable quantities of inorganic salts known to be present in atmospheric particulate.) Reported values for methylene chloride extractable average 15 weight percent, ranging from 8-22 weight percent. Values for dioxane extractable average 21 weight percent, ranging from 8-40 weight percent. Values for total extractable average 36 weight percent, ranging from 16-56 weight percent. Comparison of these values with those shown in Table 2 indicates that the model aerosols contain significantly more organic extractable matter than do atmospheric aerosols. This is especially evident when comparing values for methylene chloride extractable matter. The data support the contention that aerosols which form as a result of photochemical reactions are composed predominantly of organic matter.

In considering the structures of the hydrocarbon precursors, it is interesting to note that as the total number of carbon atoms per double-bond* decreases there is a tendency for the reaction products to have less solubility in methylene chloride and greater solubility in the polar solvent, that is, acetone or methanol (see structures p. 28).

The data suggest that under atmospheric simulation, hydrocarbons having increased numbers of double-bonds will undergo greater oxidation/degradation, yielding products which would be expected to have greater solubility in solvents of greater polarity (i.e., acetone or methanol rather than methylene chloride).

*Strict reference is made to "double-bonds" rather than "unsaturation" because the bicyclic compound α-pinene has unsaturation equivalent to a monocyclic hydrocarbon containing two double bonds.

		CARBON ATOMS PER DOUBLE-BOND
α-PINENE		(10)
CYCLOHEXENE		(6)
TOLUENE		(23)

FRACTIONATION OF AEROSOL EXTRACTS

Using the procedure described previously, methylene chloride extractable matter was fractionated into water-soluble and water-insoluble components. The water insoluble material was further fractionated into acid, neutral, and basic components. The distribution of reaction products in the three aerosol systems is shown in Table 3.

DERIVATIZATION OF AEROSOL PRODUCTS

Procedures for specific derivatization of alcohols and carbonyl compounds were investigated and the utility of this approach was considered as an aid to identification of aerosol reaction products. The various derivatization reagents described earlier were evaluated using model alcohols and carbonyl compounds, and selected reagents were applied to derivatization of reaction products.

Dithiolanes of Authentic Carbonyl Compounds

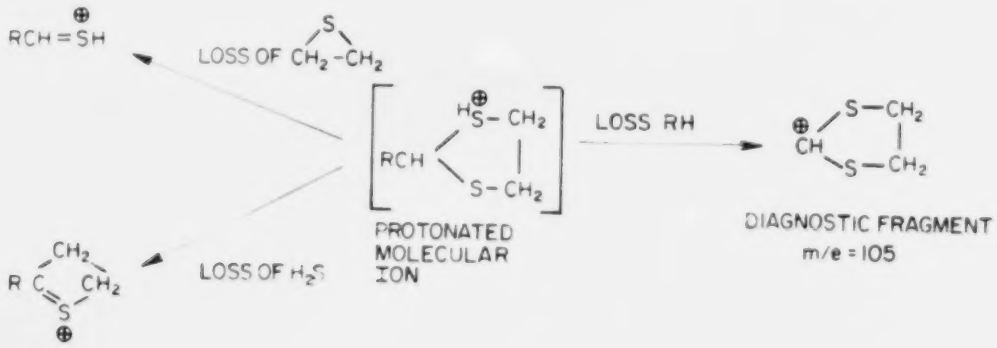
Using the previously described derivatization procedure, dithiolanes of the following authentic carbonyl compounds were prepared: n-hexaldehyde, n-heptaldehyde, 2-ethylhexaldehyde, 2-ethyl buteraldehyde, 3-hexanone, and 2,4-dimethyl-3-hexanone. The gas chromatographic retention times of the dithiolanes are significantly longer than those of the parent

Table 3. FRACTIONATION OF METHYLENE CHLORIDE EXTRACTABLE MATTER

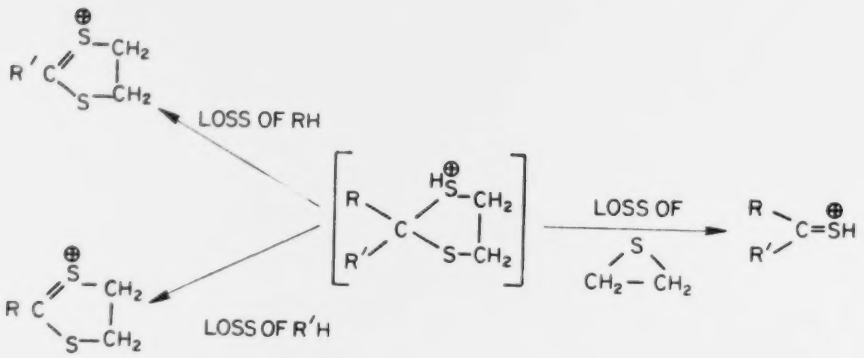
	Hydrocarbon		
	Cyclohexene	Toluene	α-Pinene
Extractable Matter Fractionated, mg	80	29	615
Water-insoluble fraction			
Acid, weight percent	8	10	52
Neutral, weight percent	3	2	17
Basic, weight percent	0.2	0.3	1
Water-soluble fraction, weight percent	66	70	27
Overall recovery, weight percent	77	82	97

carbonyl compounds. For example using a 3-m x 2-mm 3% OV-17 column programmed from 100 to 250 C at 6 C min^{-1} the retention time of 3-hexanone and 2-ethylbuteraldehyde dithiolanes are 9.3 and 11.0 minutes respectively, whereas both parent compounds elute in less than 2 minutes. Gas chromatograms of several authentic dithiolanes are shown in Figure 1. Both flame ionization and flame photometric (sulfur specific) detection were employed. The dithiolanes were further analyzed by GC-MS. Reconstructed gas chromatograms are shown in Figure 2, and chemical-ionization mass spectra are shown in Figures 3-5.

Fragmentation of aldehyde dithiolanes is highly characteristic, and is clearly diagnostic of the presence of aldehyde in the original aerosol product mixture. The fragmentation is rationalized below, and includes formation of the diagnostic fragment at m/e 105.



Fragmentation of ketone dithiolanes is similarly characteristic, but does not include appearance of the fragment at m/e 105. This can be helpful in distinguishing aldehyde and ketone dithiolanes. Fragmentation of the ketone dithiolanes is rationalized below.



Dithiolane Derivatives of α-Pinene and Cyclohexene Aerosol Products

Portions of the α-pinene and cyclohexene neutral fractions were reacted with ethanedithiol/BF_3 to obtain dithiolane derivatives. The derivatized product mixtures were analyzed by gas chromatography and GC-MS. For the sake of clarity mass spectral analyses of the derivatized aerosol products are considered as a unit under this heading. Analyses of underivatized aerosol products are considered separately in following sections for each of the three aerosol systems studied. In the present discussion, the analytical approach involving dithiolane derivatives will be evaluated.

Analyses of dithiolane derivatives for both α-pinene and cyclohexene aerosol products indicated the presence of carbonyl compounds whose molecular weights were rather low when compared to the compounds which were identified in the underivatized neutral fractions. In the cyclohexene neutral fraction, analyses of the dithiolanes indicated the presence of carbonyl compounds of the following molecular weights: 76, 84, 96, 98, 108, and 112. The α-pinene neutral fraction was

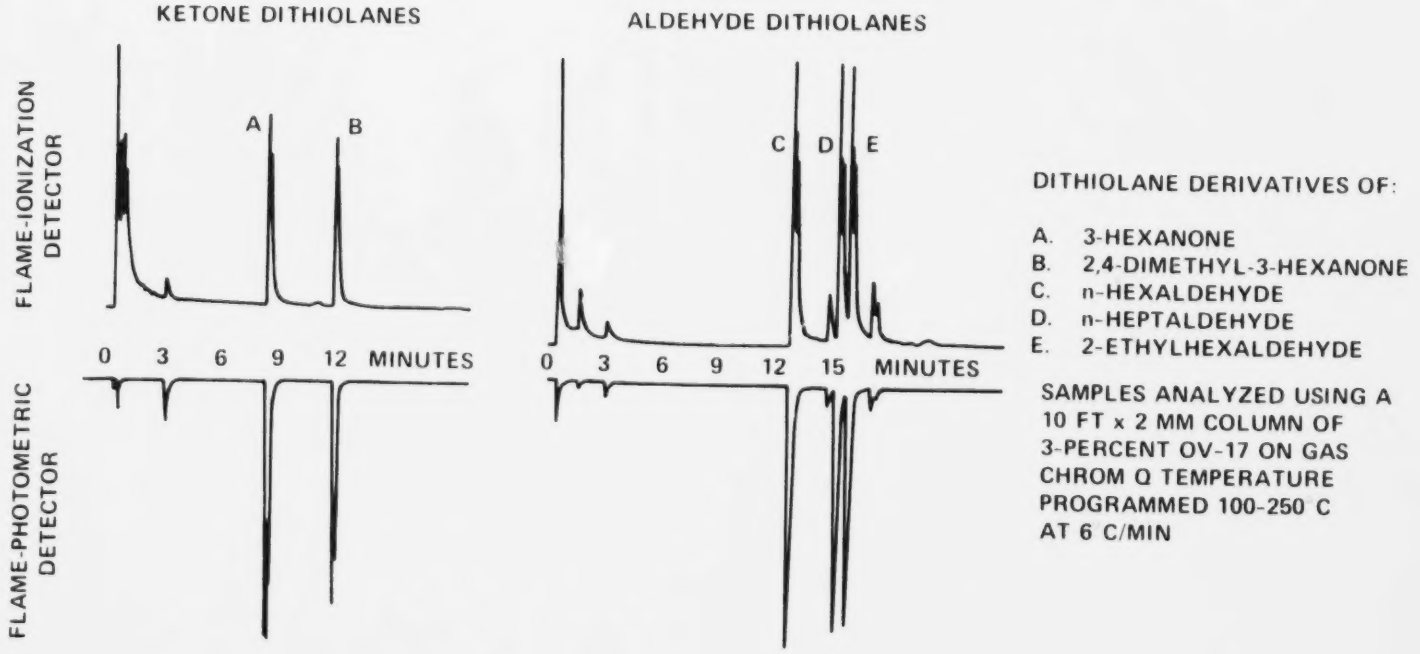
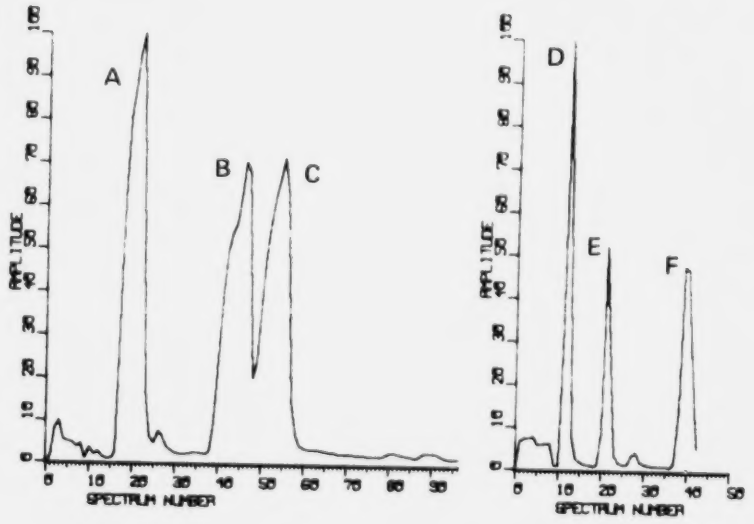


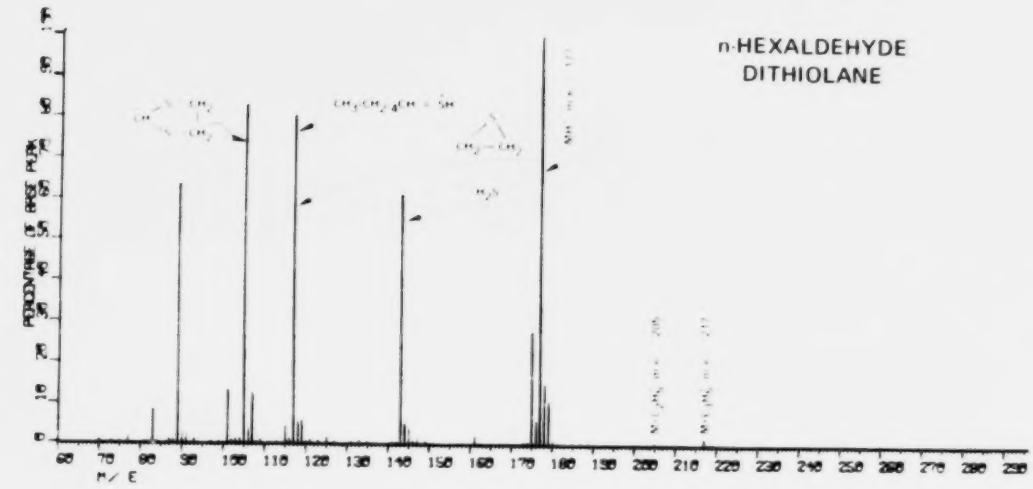
FIGURE 1. GAS CHROMATOGRAMS OF AUTHENTIC DITHIOLANES.



DITHIOLANE DERIVATIVES OF:

A. n-HEXALDEHYDE
B. n-HEPTALDEHYDE
C. 2-ETHYLHEXALDEHYDE
D. 3-HEXANONE
E. 2-ETHYLBUTYRALDEHYDE
F. 2,4-DIMETHYL-3-HEXANONE

FIGURE 2. RECONSTRUCTED GAS CHROMATOGRAMS OF AUTHENTIC DITHIOLANES.



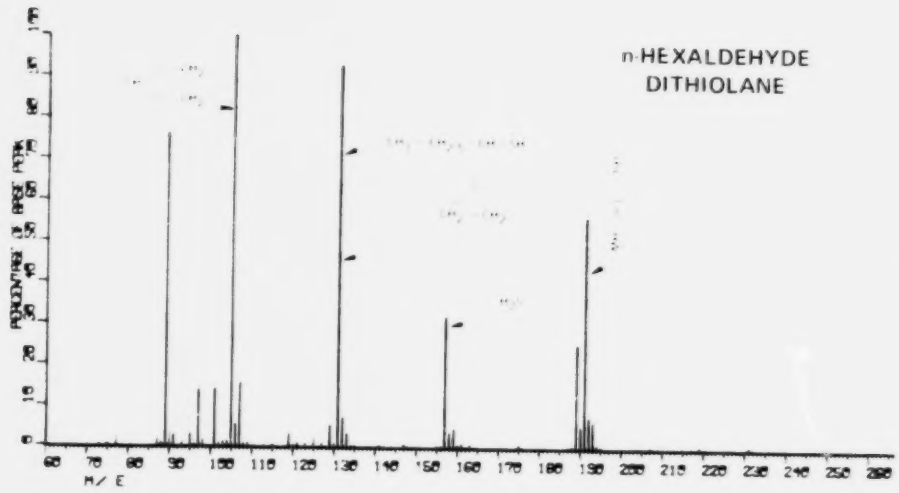
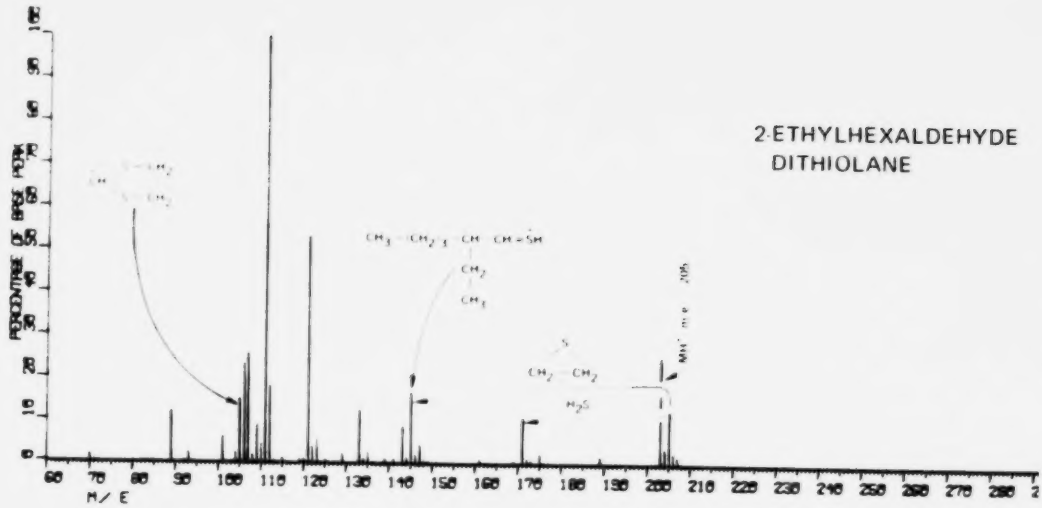


FIGURE 3. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC DITHIOLANES.

(Refer to Chromatograms in Figure 2)



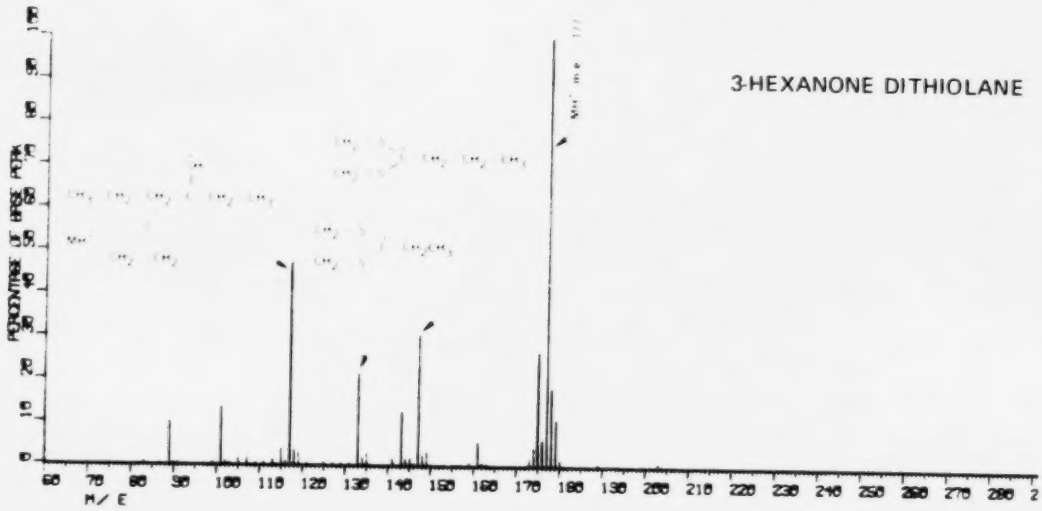


FIGURE 4. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC DITHIOLANES.

(Refer to Chromatograms in Figure 2)

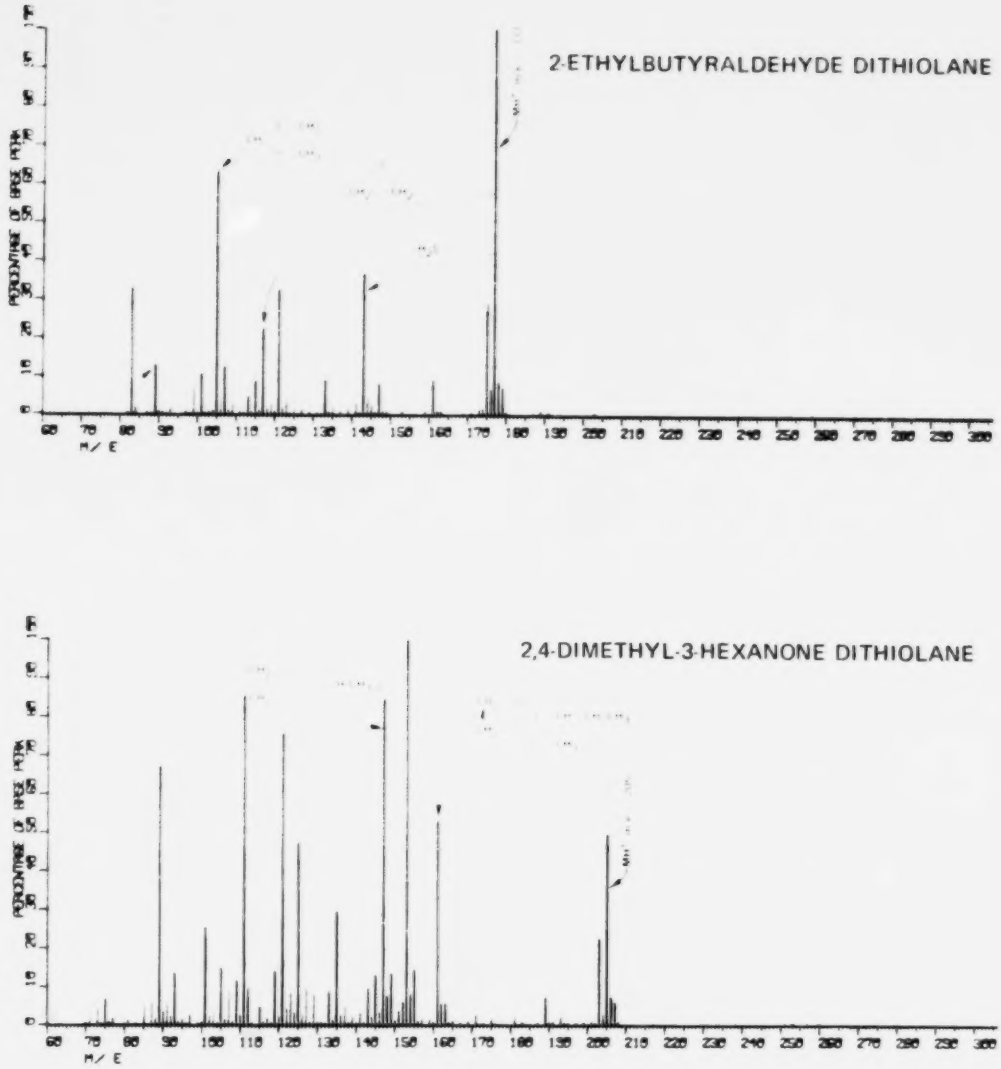
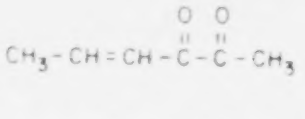


FIGURE 5. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC DITHIOLANES.

(Refer to Chromatograms in Figure 2)

indicated to contain carbonyl compounds of molecular weights, 44, 76, 78, 90, 104, and 108. The reconstructed gas chromatograms are shown in Figures 6 and 7.

Analysis of the underivatized neutral fraction of cyclohexene aerosol indicates possible formation of the products indicated below. (See mass spectra in Figures 22 and 23. These spectra are discussed in detail under the heading Cyclohexene Neutral Fraction.)



(MW = 112)

(MW = 96)

Mass spectra of the derivatives indicate the presence of dithiolanes corresponding to carbonyl compounds having the above molecular weights, 112 and 96 (peaks A and B in Figure 6). Consider the mass spectrum shown in Figure 8. This dithiolane corresponds to a derivative formed from carbonyl of molecular weight 112. Although the intense peak at m/e = 189 appears to correspond to the protonated molecular ion (dithiolane), the other rather weak peaks are not consistent with a ketone. The weak peak at m/e = 129 (loss of CH_2-CH_2) would be expected for both aldehydes and ketones, but the relatively strong peak at m/e = 105 is usually diagnostic for aldehydes.

In contrast, the mass spectrum for the underivatized product suggests the diketone, above. If the assignment of the diketone structure is correct, then the derivative mass spectrum in Figure 8 indicates the presence of an aldehyde which was not identified in the cyclohexene neutral fraction. Since this derivative spectrum gives little evidence regarding the parent carbonyl compound, any structure suggested would be purely speculative. The empirical formula is most probably $C_6H_8O_2$.

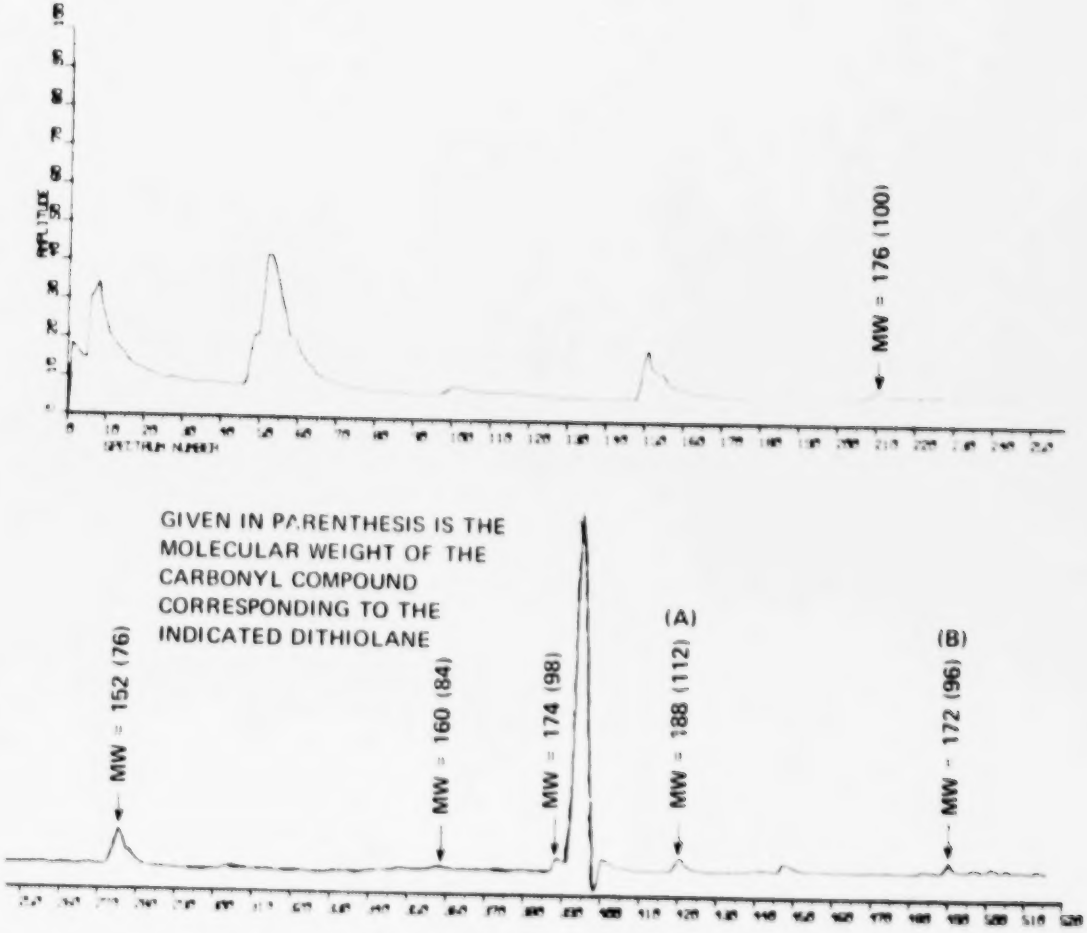

MW = 176 (100)
GIVEN IN PARENTHESIS IS THE MOLECULAR WEIGHT OF THE CARBONYL COMPOUND CORRESPONDING TO THE INDICATED DITHIOLANE
MW = 152 (76)
MW = 160 (84)
MW = 174 (98)
(A)
MW = 188 (112)
(B)
MW = 172 (96)

FIGURE 6. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION DITHIOLANE DERIVATIVES. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

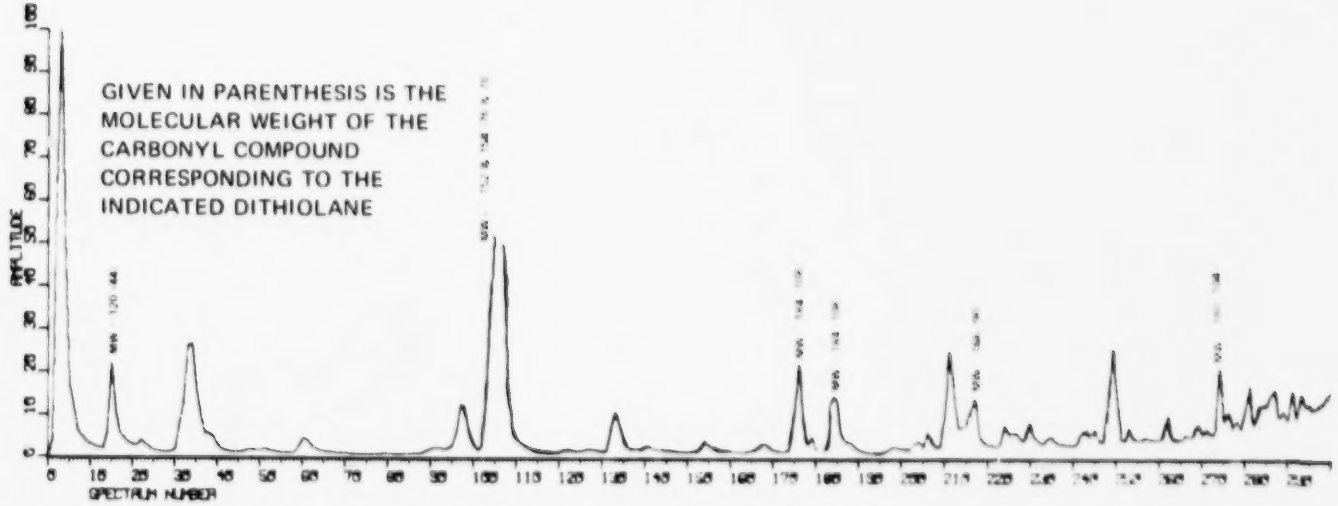


FIGURE 7. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION DITHIOLANE DERIVATIVES. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

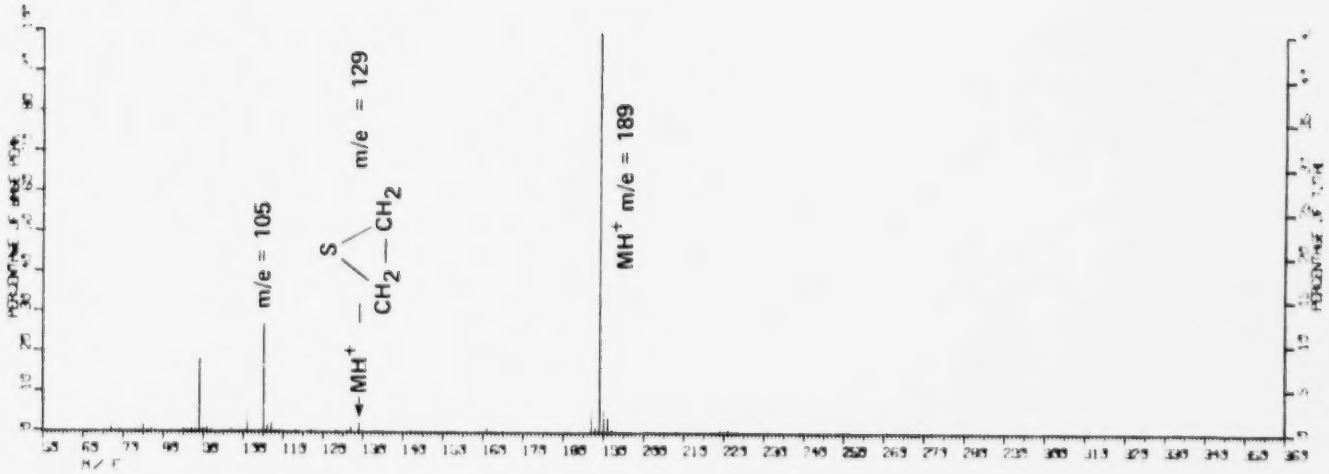


FIGURE 8. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION DITHIOLANE DERIVATIVES. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK A.

(Refer to Chromatograms in Figure 6)

Consider the mass spectrum shown in Figure 9. This dithiolane corresponds to a derivative formed from carbonyl of molecular weight 96. The peak at m/e 173 corresponds to the protonated parent ion. The peak at m/e 113 corresponds to loss of $CH_2\overset{S}{\diagdown}\!\!-\!\!\diagup CH_2$. The complete absence of a peak at m/e 105 would suggest that the parent compound may be a ketone. However, we have been unable to explain the other strong peaks at m/e = 89, 101, and 119 in these terms. It is possible that these fragments represent interference arising from other compounds simultaneously eluted. Thus, it is not clear whether the dithiolane corresponds to a derivative of the indicated aldehyde, or to a derivative of a carbonyl compound that was not otherwise detected in the cyclohexene neutral fraction.

Dithiolane derivatives of the α-pinene neutral fraction were prepared and analyzed by GC-MS. No carbonyl compounds found in the α-pinene neutral fraction corresponded with the rather low molecular weight derivatives found. The absence of higher molecular weight carbonyl derivatives may indicate that these species failed to elute under the chromatographic conditions employed, as there is no clear reason why they should not be formed.

In conclusion, it appears that use of dithiolane derivatives is a potentially useful approach to aid in characterization of carbonyl reaction products. In order to utilize this approach, gas chromatographic conditions will be determined which permit elution of the higher molecular weight dithiolanes.

Perfluoroacyl and Phosphate Derivatives of Authentic Alcohols

For convenience, the previously described candidate reagents for derivatization of alcohols are listed below:

1. Trifluoracetyl imidazole
2. Heptafluorobutyryl imidazole
3. Heptafluorobutyryl chloride
4. Pentafluorobenzoyl chloride
5. Diethylchlorophosphate.

Evaluation of Reagents 1-3 indicated that although the desired esters are formed with various model alcohols, the product esters are insufficiently stable and are hydrolyzed back to free alcohol and perfluorocarboxylic acid during aqueous work-up of the reaction mixture. Gas chromatographic analyses of the reaction mixtures without aqueous work-up proved to be troublesome in that excess derivatization reagent was deposited at the head of the GC column, leading to column degradation and irregular results.

Reagent 4 was shown to be sufficiently reactive toward various primary and secondary alcohols. Excess reagent was easily hydrolyzed during work-up without decomposition of product esters. The product esters were shown to be suitable for specific detection by electron-capture gas chromatography.

Simultaneous with evaluation of Reagent 4, diethylchlorophosphate, Reagent 5, was studied. This reagent has properties similar to those of the carboxylic acid chlorides, and was shown to react with various primary and secondary alcohols. Reaction with a tertiary alcohol (3-methyl-3-hexanol) was also attempted, but no product was observed by gas chromatography. The phosphate derivatives produced can be specifically detected using flame-photometric gas chromatography. Thus preliminary analysis of such alcohol derivatives can be conducted using the same instrument as is used for analysis of dithiolane derivatives of carbonyl compounds. In view of this fact, evaluation of diethylchlorophosphate was emphasized.

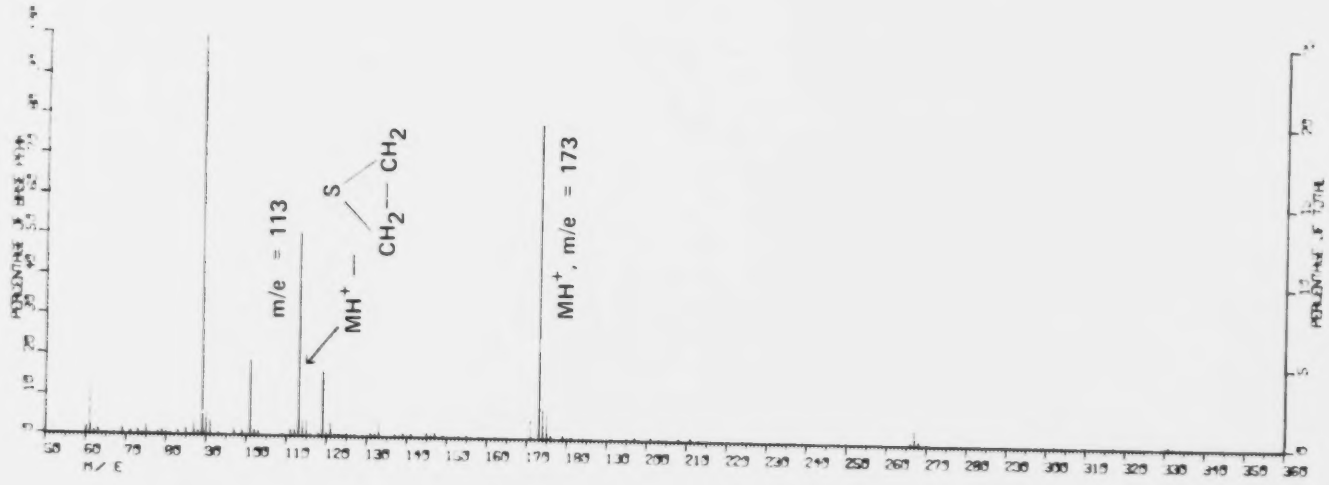
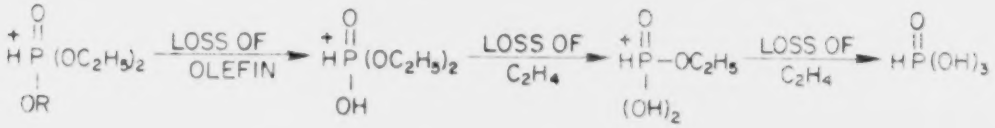


FIGURE 9. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION DITHIOLANE DERIVATIVES. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK B.

(Refer to Chromatogram in Figure 6)

Phosphate derivatives of various primary and secondary alcohols were prepared and analyzed by GC-MS. A reconstructed gas chromatogram for the derivatives of isopropanol, 1-pentanol, 3-hexanol, and 1-decanol is shown in Figure 10. The mass spectra are shown in Figures 11 and 12.

A clearly characteristic fragmentation pattern is evident in the spectra. It appears that initial fragmentation of the phosphate ester involves loss of olefin corresponding to the parent alcohol. Subsequent fragmentation was identical for all of the derivatives, and simply involved two successive losses of ethylene.



Phosphate Derivatives of α-Pinene Aerosol Products

A portion of the α-pinene neutral fraction was derivatized with diethylchlorophosphate, and was analyzed by GC-MS. The reconstructed gas chromatogram is shown in Figure 13. The chromatographic resolution of the derivatives is poor. Examination of typical spectra shown in Figure 14 reveal very characteristic phosphate fragmentation with peaks at m/e 155, 127, and 99. It was nevertheless, not possible to identify significant parent or adduct peaks in these spectra. Consequently, the molecular weight of the products could not be determined. Examination of spectra of authentic phosphate derivatives indicates that even when a strong protonated parent ion is observed, fragmentation is rather uninformative. At best, it appears that preparation and analysis of phosphate derivatives can aid in establishing the presence of alcohol and the molecular weight of an aerosol product. In light of these findings, this approach to specific derivatization of alcohols was discontinued. Limited future work may be undertaken using Reagent 4 above.

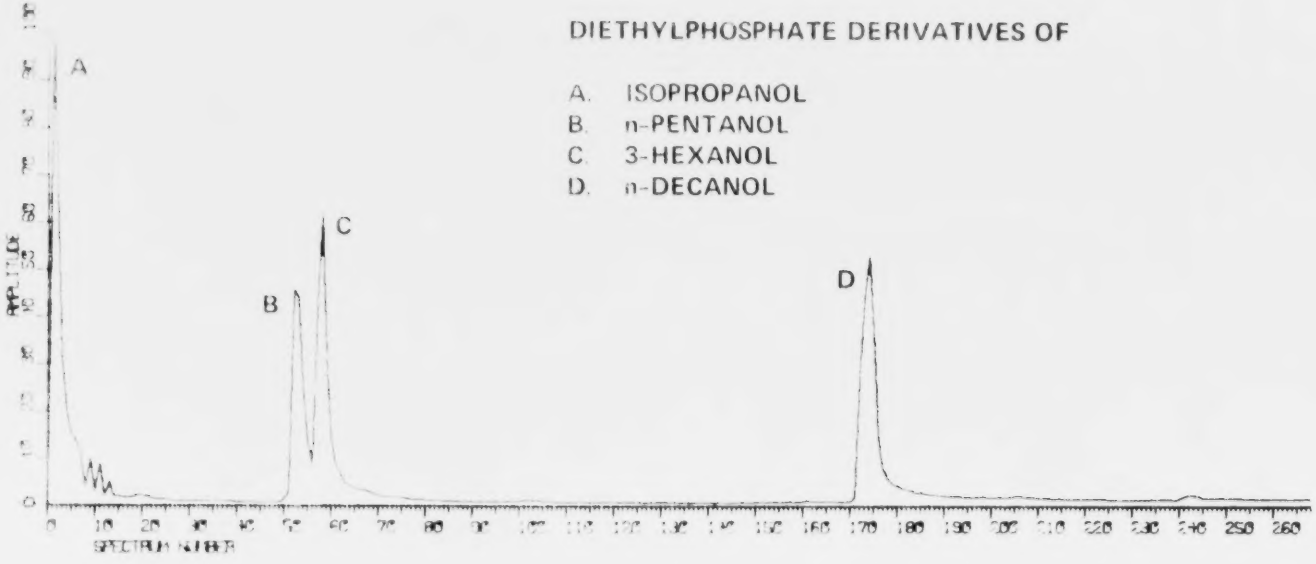


FIGURE 10. RECONSTRUCTED GAS CHROMATOGRAM OF DIETHYLPHOSPHATE DERIVATIVES OF AUTHENTIC ALCOHOLS.

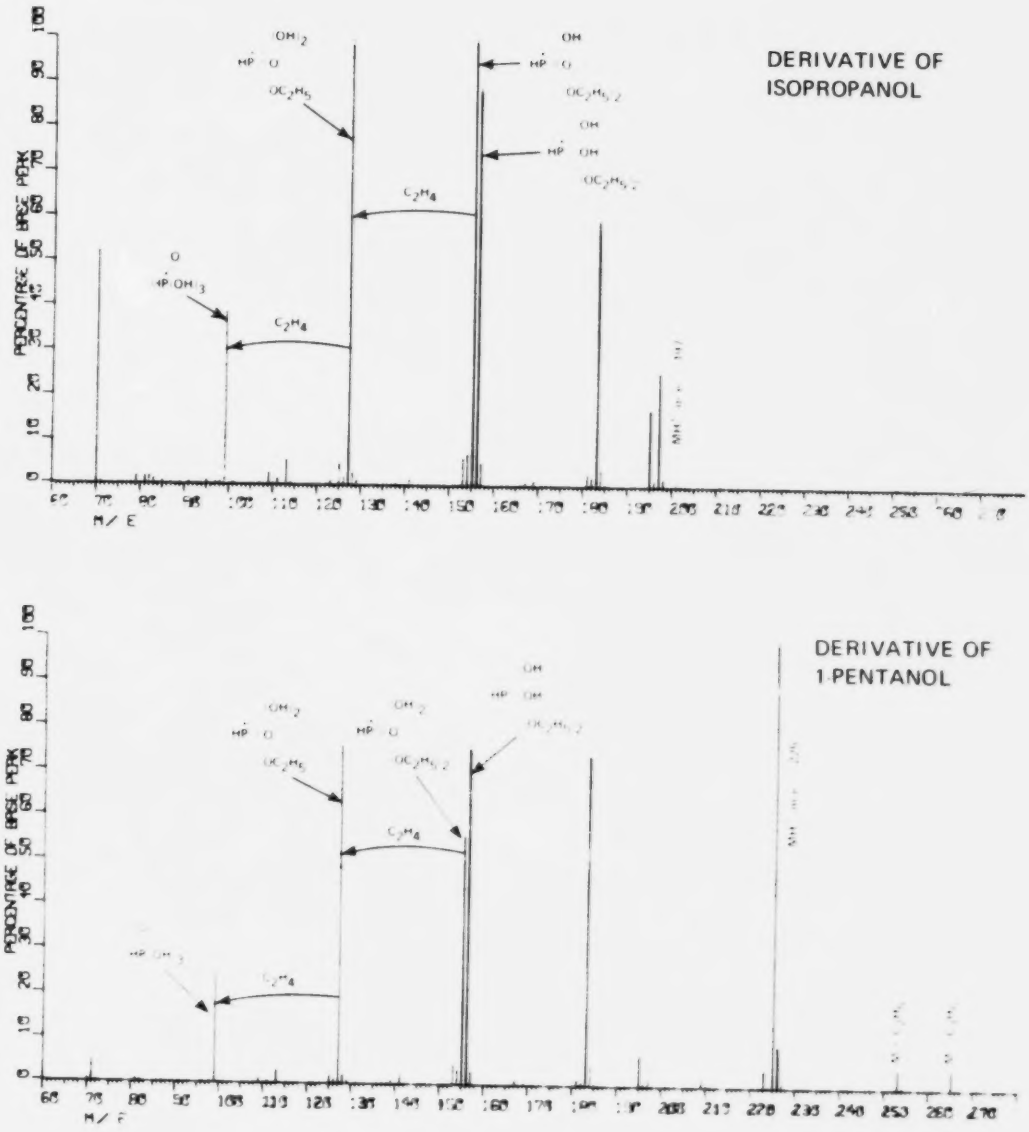


FIGURE 11. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF DIETHYLPHOSPHATE DERIVATIVES OF AUTHENTIC ALCOHOLS.

(Refer to Chromatogram in Figure 10)

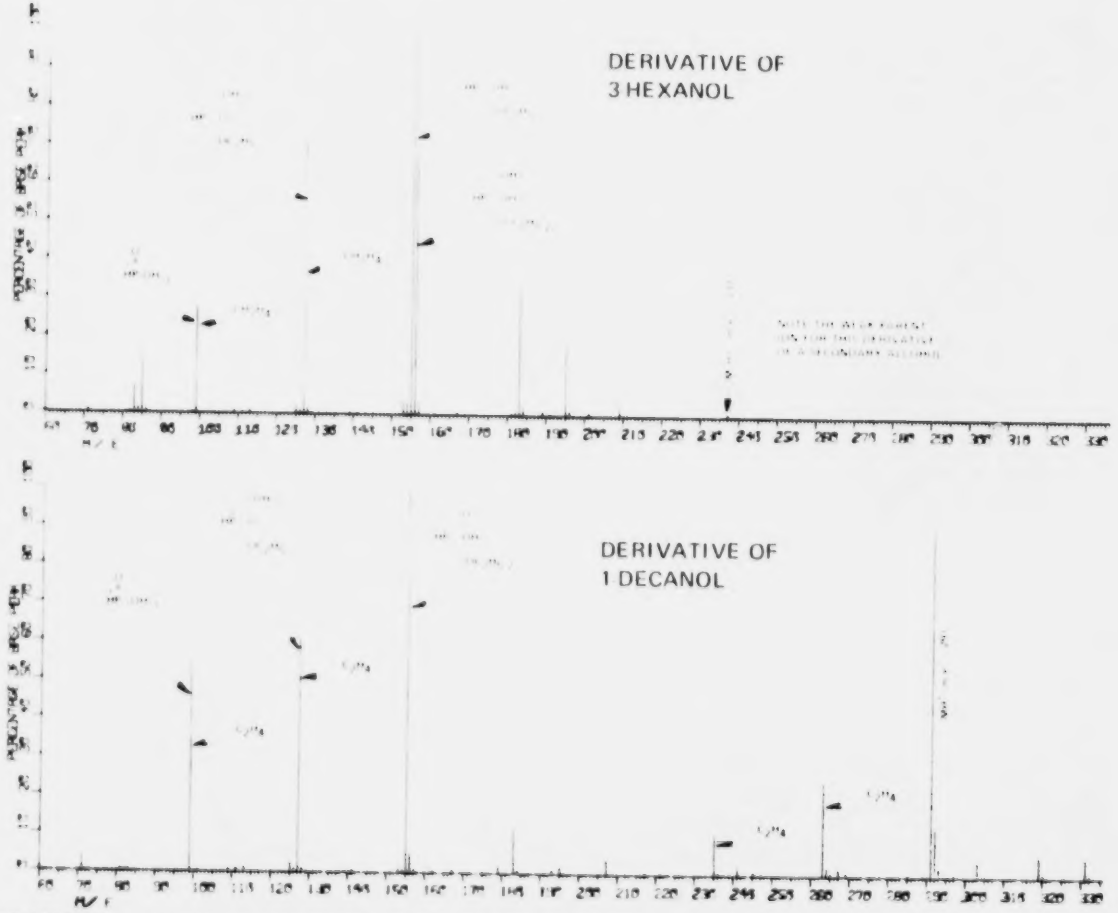


FIGURE 12. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF DIETHYLPHOSPHATE DERIVATIVES OF AUTHENTIC ALCOHOLS.

(Refer to Chromatogram in Figure 10)

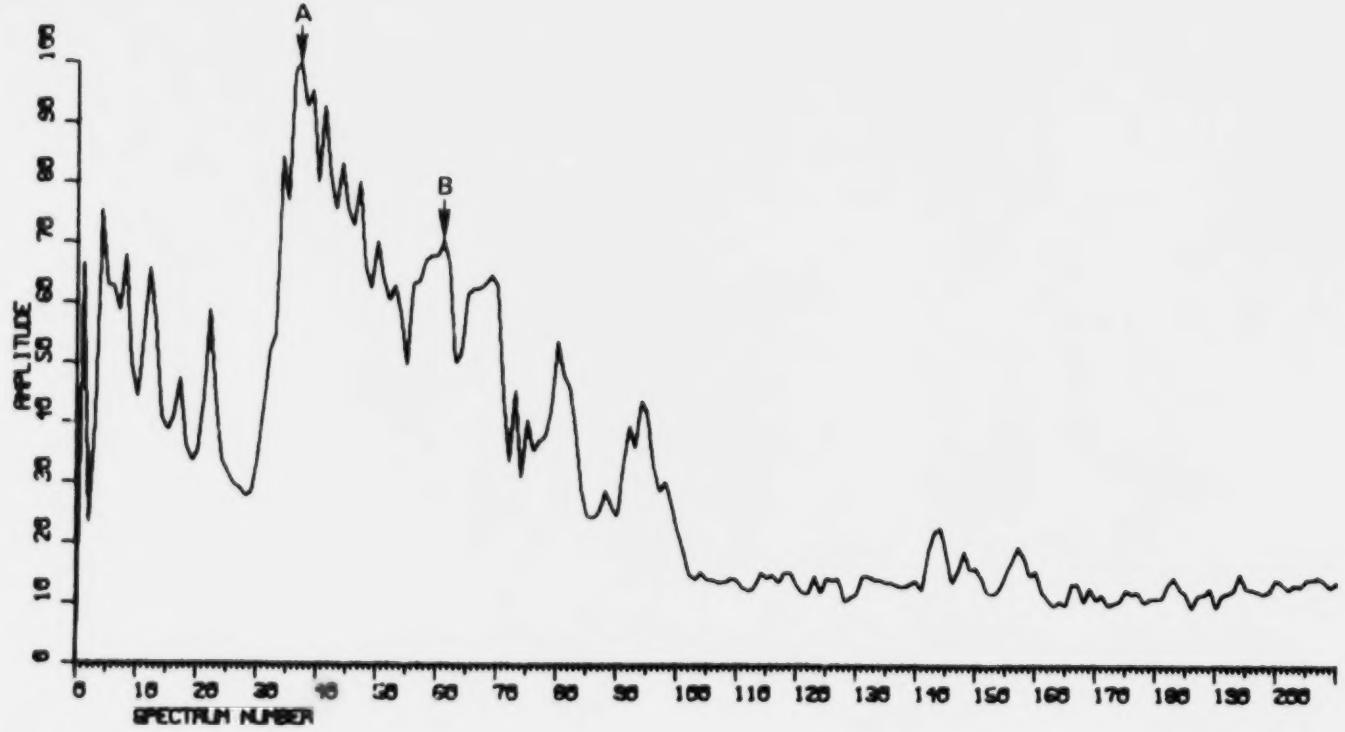


FIGURE 13. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION DIETHYLPHOSPHATE DERIVATIVES. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

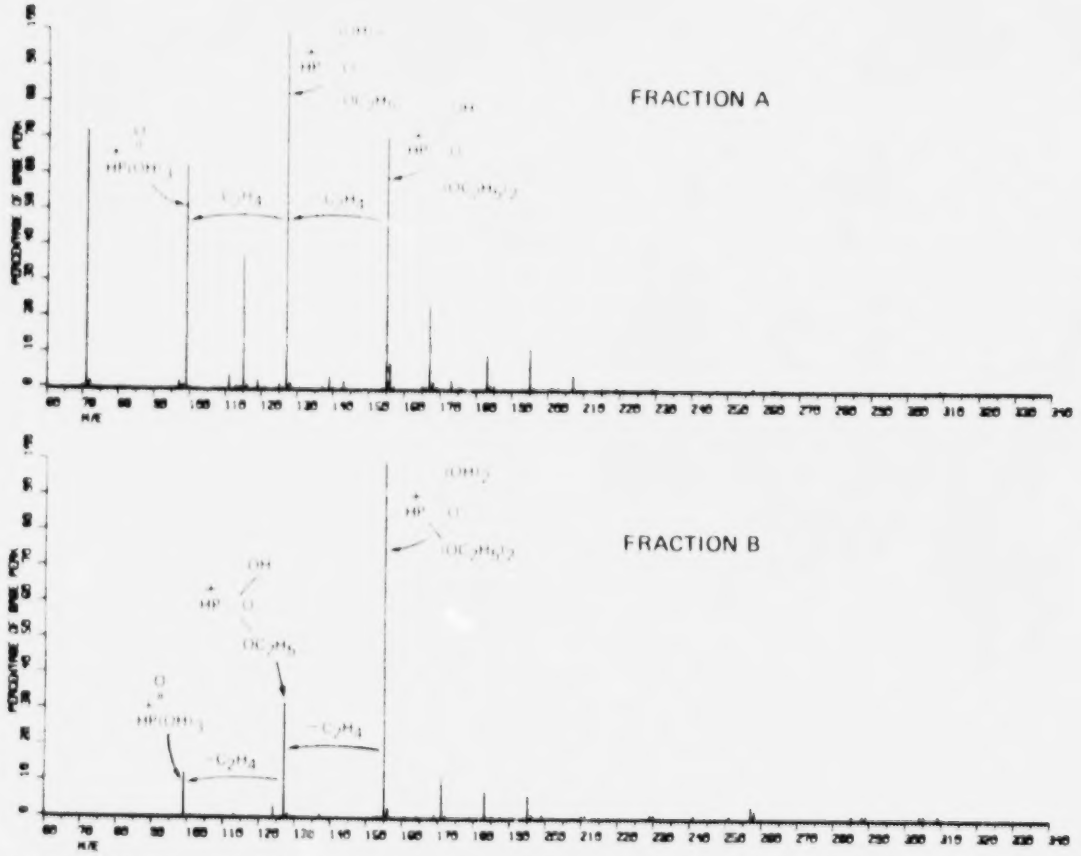


FIGURE 14. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION DIETHYLPHOSPHATE DERIVATIVES. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAKS A AND B.

(Refer to Chromatogram in Figure 13)

ANALYSIS OF CYCLOHEXENE AEROSOL

Cyclohexene Aerosol Acid Fraction

The water-insoluble acid fraction of cyclohexene aerosol was isolated as described above. The mixture was treated with diazomethane, and the resulting methyl esters were analyzed by gas chromatography and GC-MS. The reconstructed gas chromatogram is shown in Figure 15. Tentative identifications have been made on the basis of mass spectra for the indicated chromatographic components.

The mass spectrum corresponding to chromatographic peak C is shown in Figure 16. The product is tentatively identified as the six membered aldehyde-acid shown. There is a moderately strong peak assigned as protonated parent ion at m/e 145. Fragmentation peaks consistent with loss of CH_3OH and loss of CH_3CHO are observed at m/e 113 and 101, respectively. Somewhat less prominent is a peak corresponding to loss of $HCOOCH_3$ (methyl formate). This can be seen at m/e 85. Loss of $HCOOCH_3$ and CH_3OH are diagnostic of carboxylic acid-methyl esters. Loss of CH_3CHO is diagnostic of aldehydes.

The mass spectrum in Figure 17 corresponds to chromatographic peak A. The tentatively identified aldehyde-acid is shown in the figure, and corresponds to the next lower homologue of the product considered in the case above. There is a moderately strong peak assignable to protonated parent ion at m/e 131 and weak adduct peak at m/e 159 ($M + C_2H_5^+$). Prominent fragmentation peaks consistent with loss of CH_3OH and loss of CH_3CHO are observed at m/e 99 and 87, respectively. Less prominent, at m/e 71, is the fragment corresponding to loss of $HCOOCH_3$.

Consider next the mass spectrum shown in Figure 18, corresponding to chromatographic peak B. The compound is tentatively identified as the methyl ester of 5-hydroxypentanoic acid. The moderately strong peak at m/e 133 is assigned as protonated parent ion. The weak peak

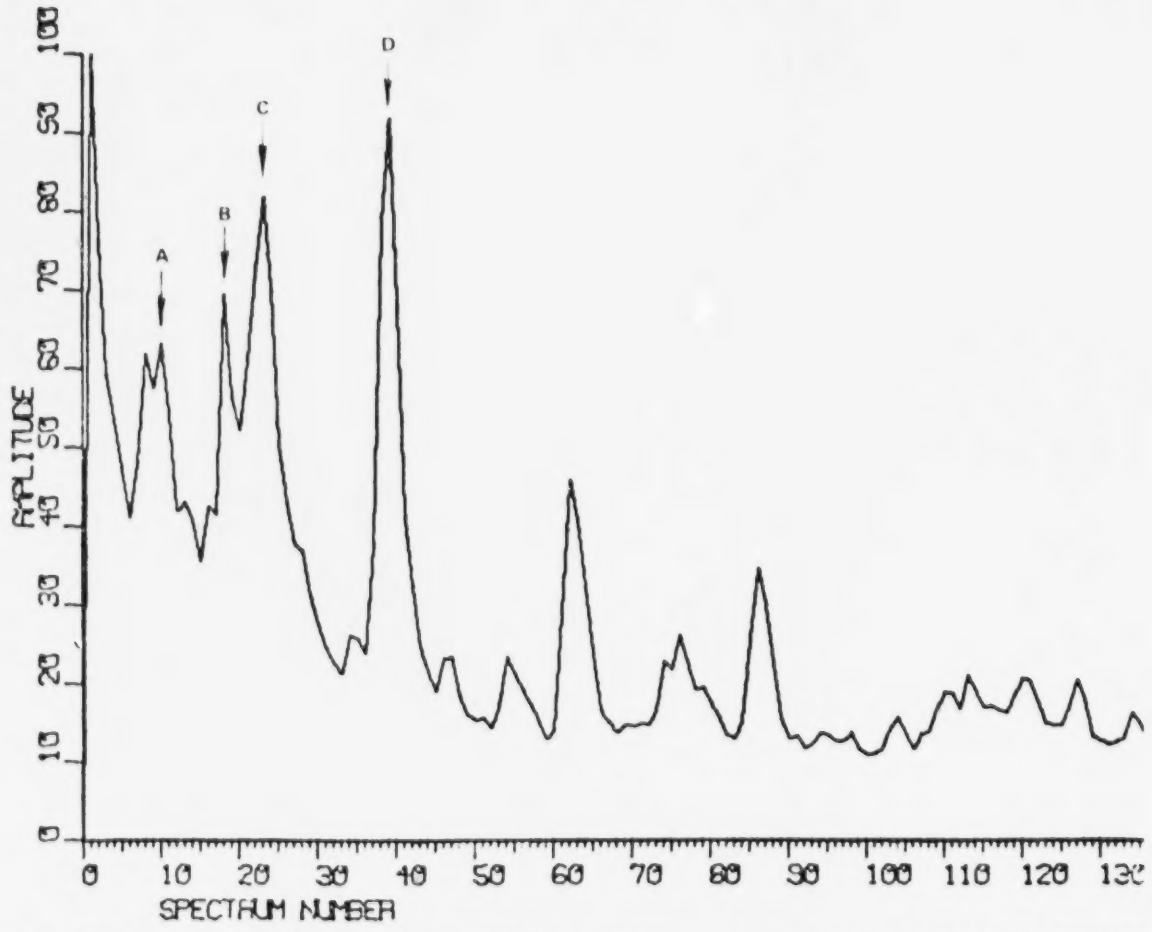


FIGURE 15. ANALYSIS OF CYCLOHEXENE AEROSOL, ACID FRACTION METHYL ESTERS. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

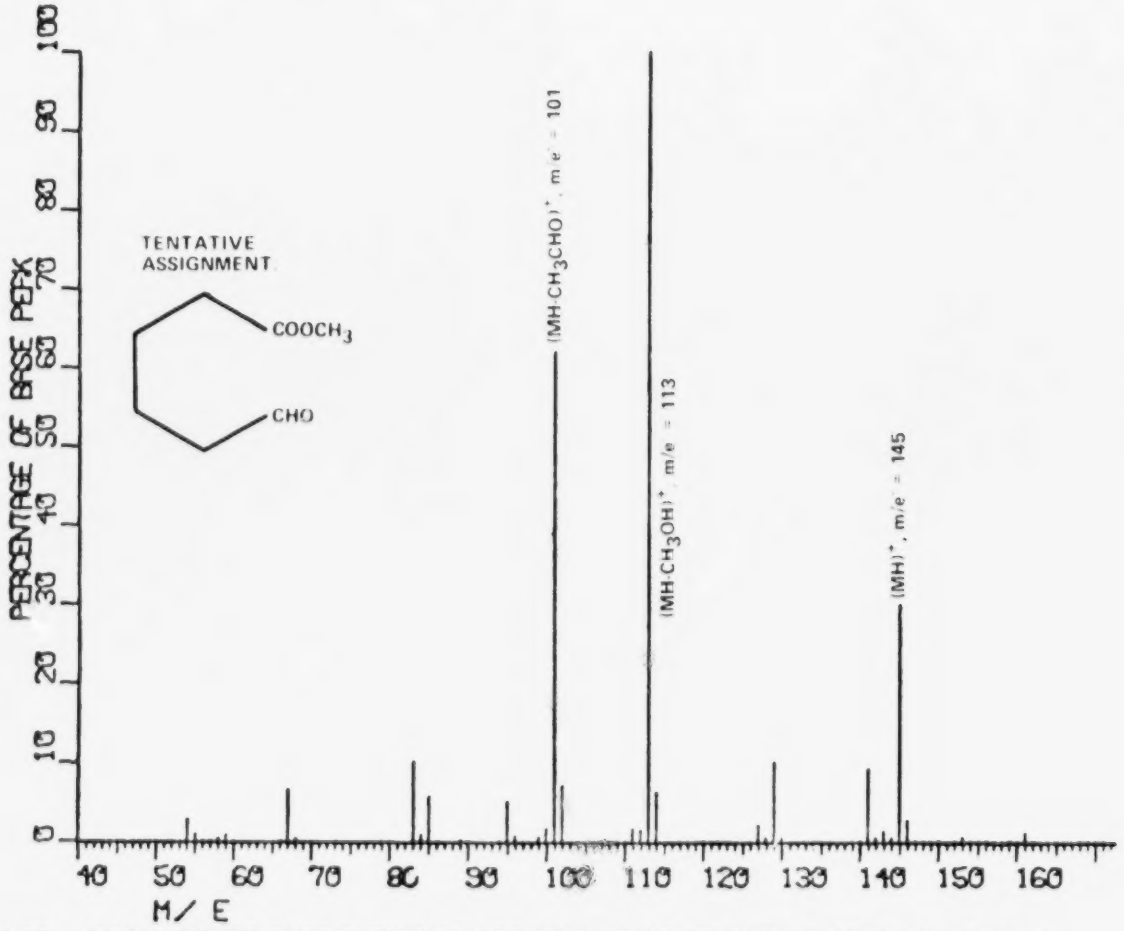


FIGURE 16. ANALYSIS OF CYCLOHEXENE AEROSOL, ACID FRACTION METHYL ESTERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK C.

(Refer to Chromatogram in Figure 15)

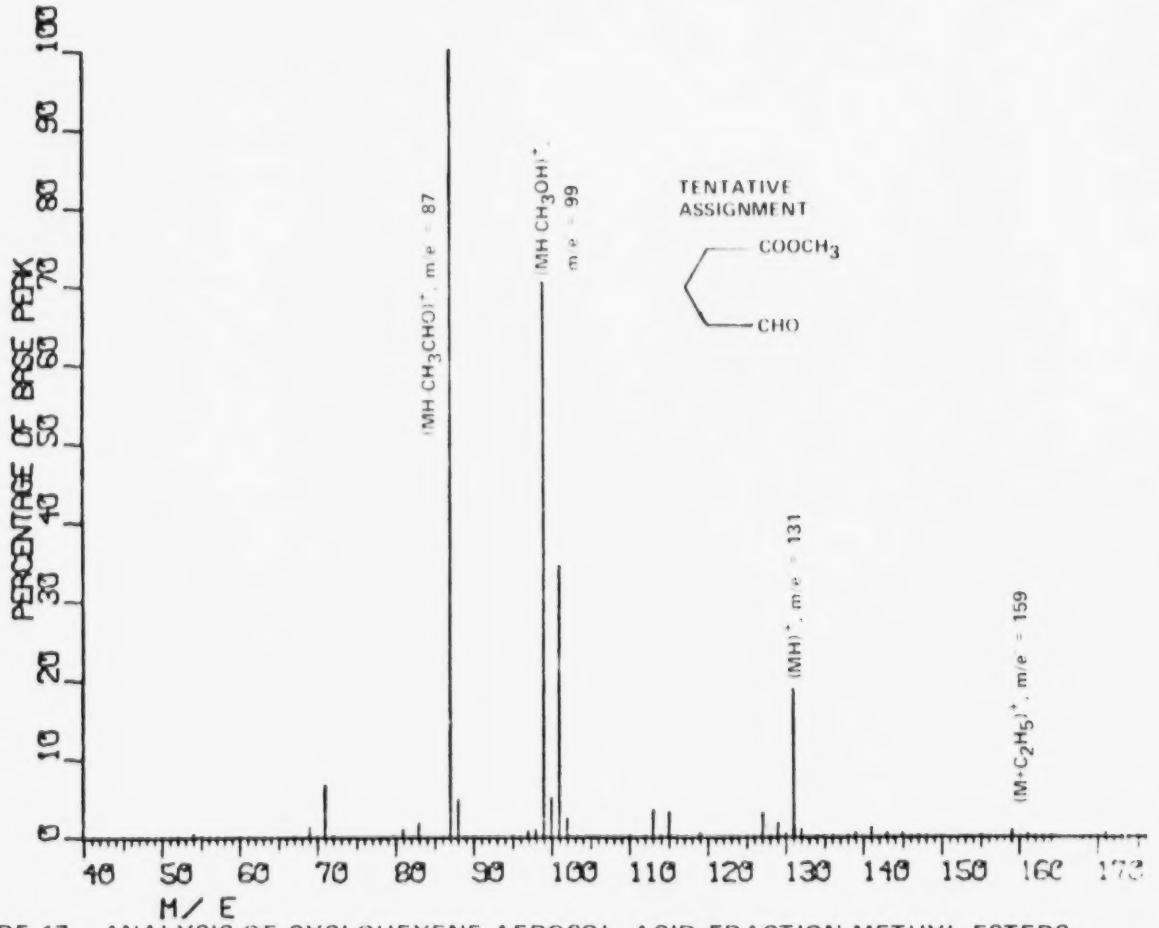


FIGURE 17. ANALYSIS OF CYCLOHEXENE AEROSOL, ACID FRACTION METHYL ESTERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK A.

(Refer to Chromatogram in Figure 15)

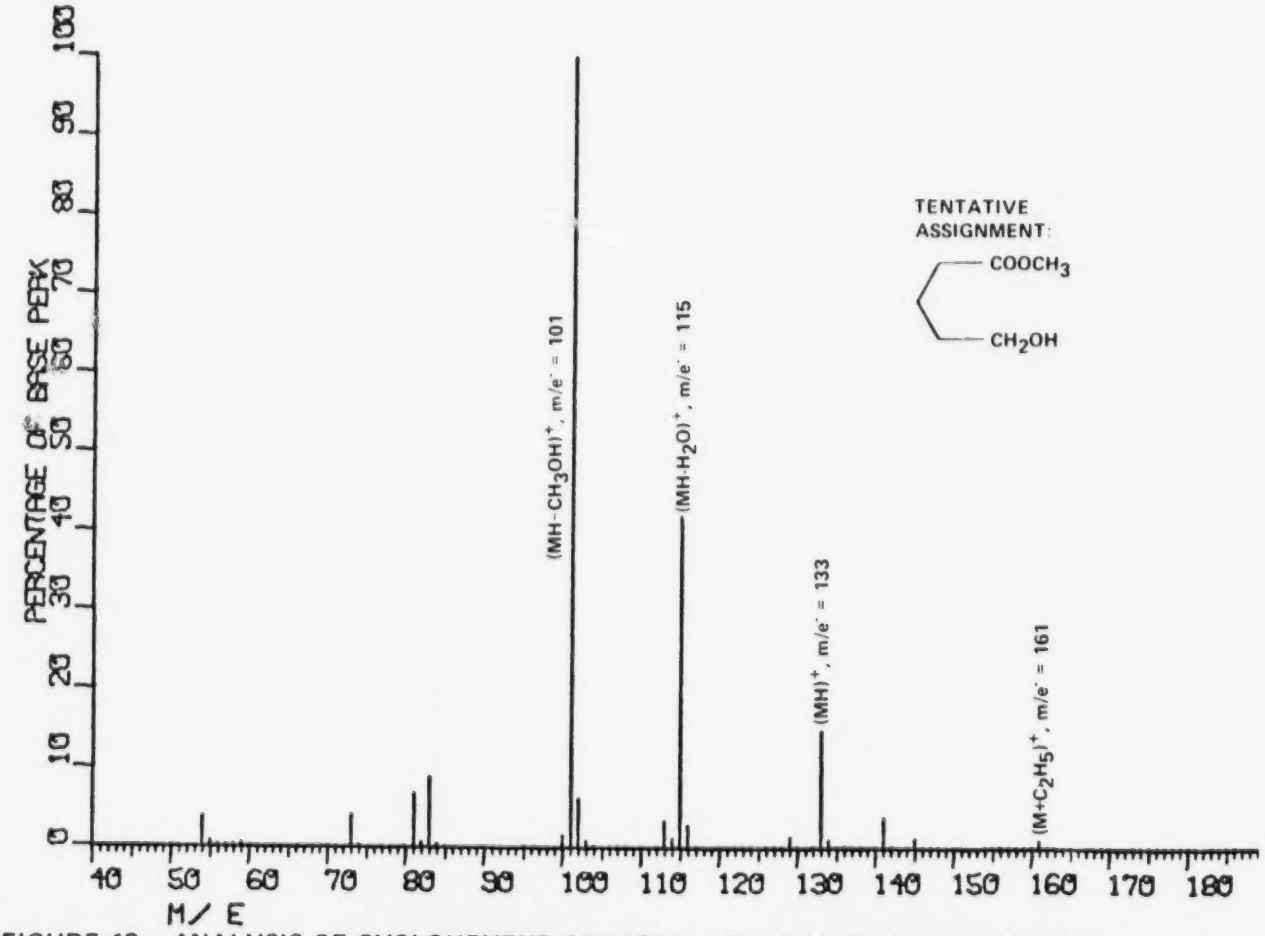


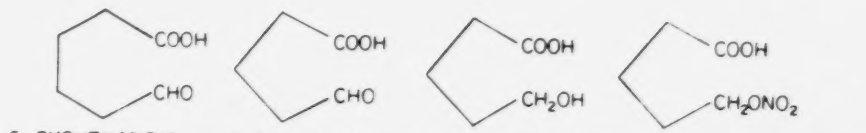
FIGURE 18. ANALYSIS OF CYCLOHEXENE AEROSOL, ACID FRACTION METHYL ESTERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK B.

(Refer to Chromatogram in Figure 15)

at m/e 161 is consistent with adduct ion ($M + C_2H_5^+$). Prominent fragmentation peaks consistent with loss of H_2O and loss of CH_3OH are observed at m/e 115 and 101 respectively, while the less intense peak at m/e 73 corresponds to loss of $HCOOCH_3$.

Finally, consider the mass spectrum shown in Figure 19, corresponding to chromatographic peak D. This rather interesting product is tentatively identified as the 5-nitrate ester of the product considered in the case above. The peak for protonated parent-ion is observed at m/e 178. Prominent fragmentation peaks consistent with loss of CH_3OH and loss of HNO_3 are observed at m/e 146 and 115, respectively.

In summary, four bifunctional carboxylic acids indicated below have been tentatively identified in the acid fraction of cyclohexane aerosol. Oxidative cleavage of cyclohexane in the presence of ozone and hydrogen peroxide can reasonably be expected to yield 6-oxohexanoic acid. (Hydrogen peroxide has been observed in the atmosphere and in model systems[61].) Further oxidative decarboxylation might then yield the 5-oxopentanoic acid. The 5-hydroxypentanoic acid might be formed via disproportionation from pentanedialdehyde.



6-OXOHEXANOIC ACID | 5-OXOPENTANOIC ACID | 5-HYDROXYPENTANOIC ACID | 5-NITRATOPENTANOIC ACID

Formation of 5-nitratopentanoic acid is of interest for a number of reasons. First, the presence of nitrate esters in the atmosphere could be significant from the standpoint of health effects. In general,

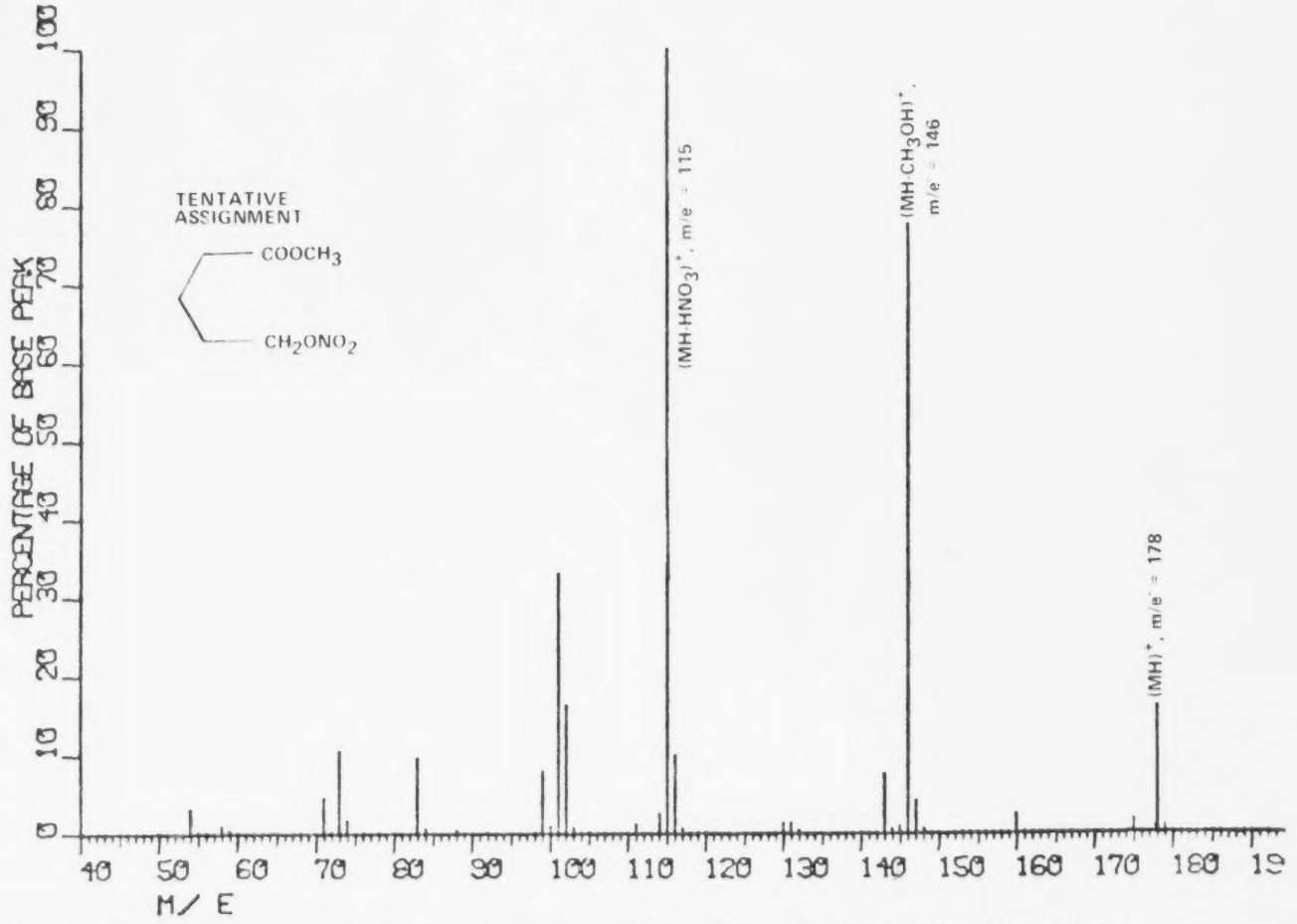
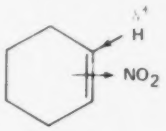


FIGURE 19. ANALYSIS OF CYCLOHEXENE AEROSOL, ACID FRACTION METHYL ESTERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK D.

(Refer to Chromatograms in Figure 15)

the fate of nitrogen oxides in the atmosphere has long been a question of interest. Formation of nitrate esters represents an additional "nitrogen sink" in the atmosphere. Currently there is considerable controversy regarding the formation mechanism of peroxyacylnitrate (PAN) in the atmosphere. Nevertheless, it is interesting to speculate as to possible formation mechanism for nitrate esters. This might involve the formation of a charge transfer complex between the olefin and NO_2, which would result in enhanced reactivity of the vinyl hydrogen.



CYCLOHEXENE – NO_2 CHARGE TRANSFER COMPLEX

One can speculate that free radical oxidation could result in a peroxy species at the vinyl hydrogen, and it is possible that a concerted induced homolytic peroxy fission followed by addition of the complexed NO_2 could result in a nitrate ester. This suggested mechanism is somewhat similar to that previously proposed for cyclic sulfite formation from olefins and sulfur dioxide[48]. It is also possible that the mechanism is entirely free radical in nature, as has been suggested for PAN formation. However, in the absence of additional supportive data, further mechanistic suggestions appear to be unwarranted.

Cyclohexene Aerosol Neutral Fraction

The water insoluble neutral fraction of cyclohexene aerosol was isolated as described previously, and was analyzed by gas chromatography and GC-MS. Both methane and helium chemical ionization spectra will be considered. The reconstructed gas chromatogram for methane CI is shown in Figure 20; that for helium is shown in Figure 21.

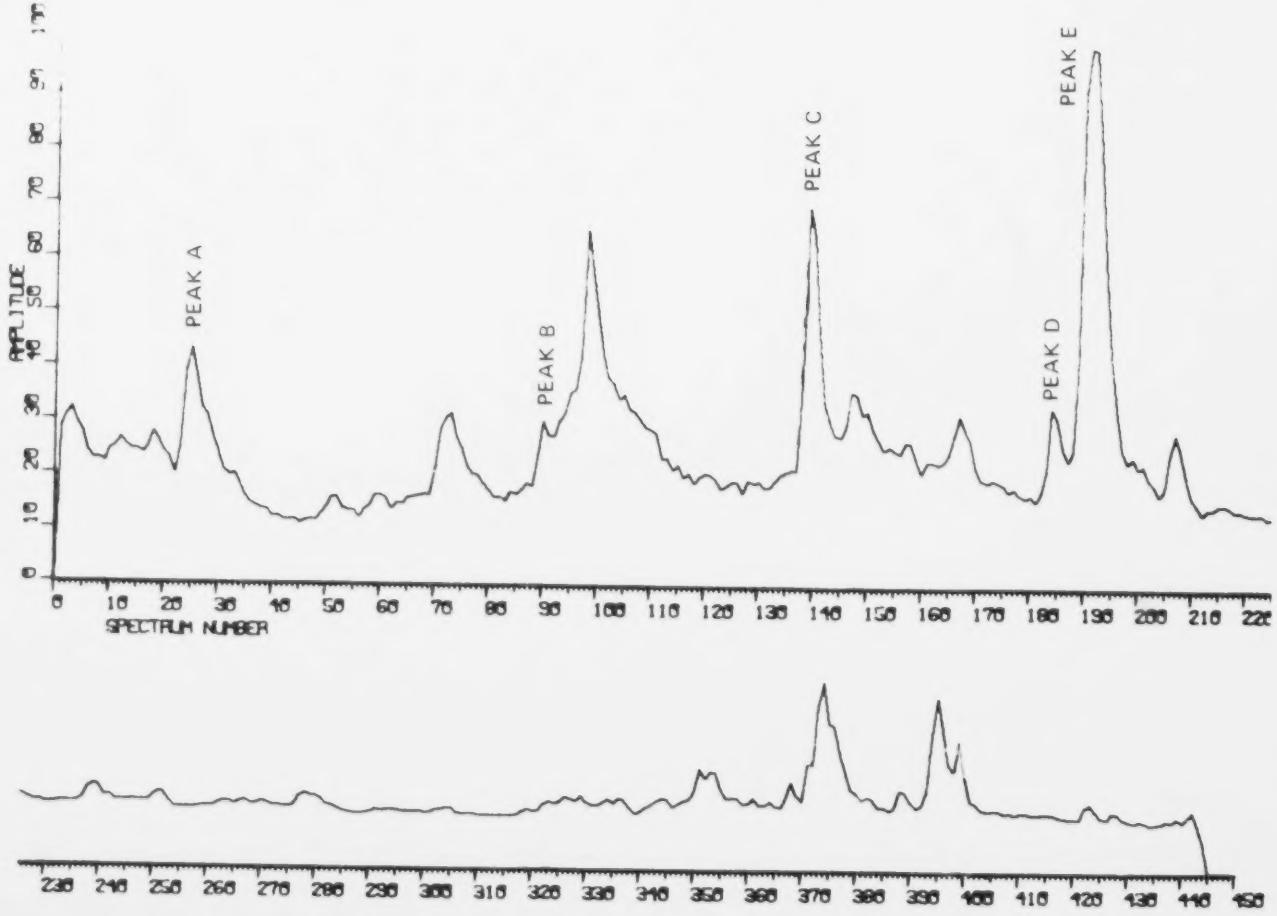


FIGURE 20. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

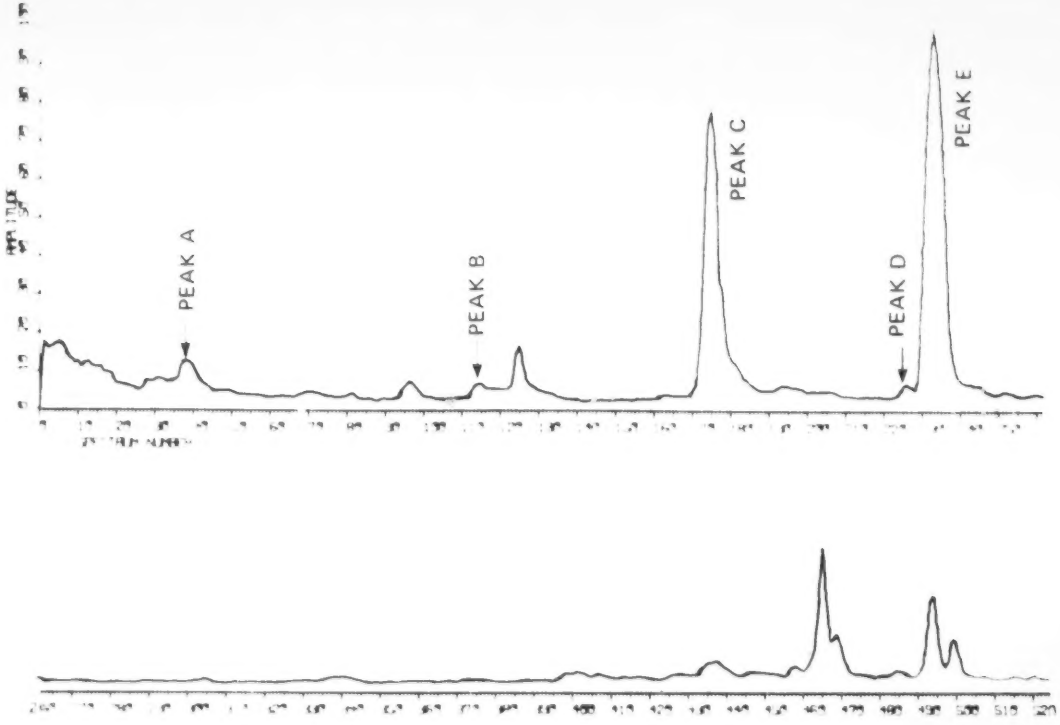
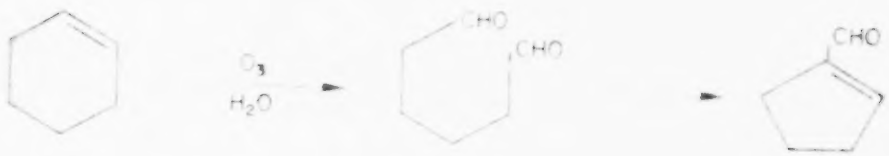


FIGURE 21. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION. RECONSTRUCTED GAS CHROMATOGRAM FOR HELIUM CI-MS.

It should be pointed out that chromatographic peaks C and E represent the only notable case of contamination observed during this year's study. The two components have been identified as dimethyl gluturate and dimethyl adipate. Although the source of contamination remains uncertain, these two compounds are widely used industrial plasticizers. Glutaric or adipic acids might be expected in the acid fraction but should not appear in the neutral fraction. Moreover, the neutral fraction was never treated with diazomethane, thus methyl esters could not have been formed from aerosol products.

Of the neutral aerosol products for which possible structures have been presented, the most interesting is considered in Figure 22. This mass spectrum corresponds to chromatographic peak A. The several structures shown are consistent with both the methane and helium chemical ionization spectra. The methane spectrum suggests a compound of molecular weight 96. Peaks are observed consistent with parent ion, protonated parent ion, and parent minus hydride ion at m/e 96, 97, and 95 respectively. Peaks consistent with addact ions are observed at m/e 125 and 137 ($M + C_2H_5^+$) and ($M + C_3H_5^+$). In the helium mass spectrum peaks are observed consistent with parent ion at m/e 96, and respectively, loss of H, HDO, and (HCO + C_2H_3) from the parent ion, at m/e 95, 67, and 55, respectively.

As indicated below, a cyclic unsaturated aldehyde might be expected to form upon internal aldol condensation and dehydration of hexane dialdehyde. Hexane dialdehyde is known to form upon ozonolysis of cyclohexene.



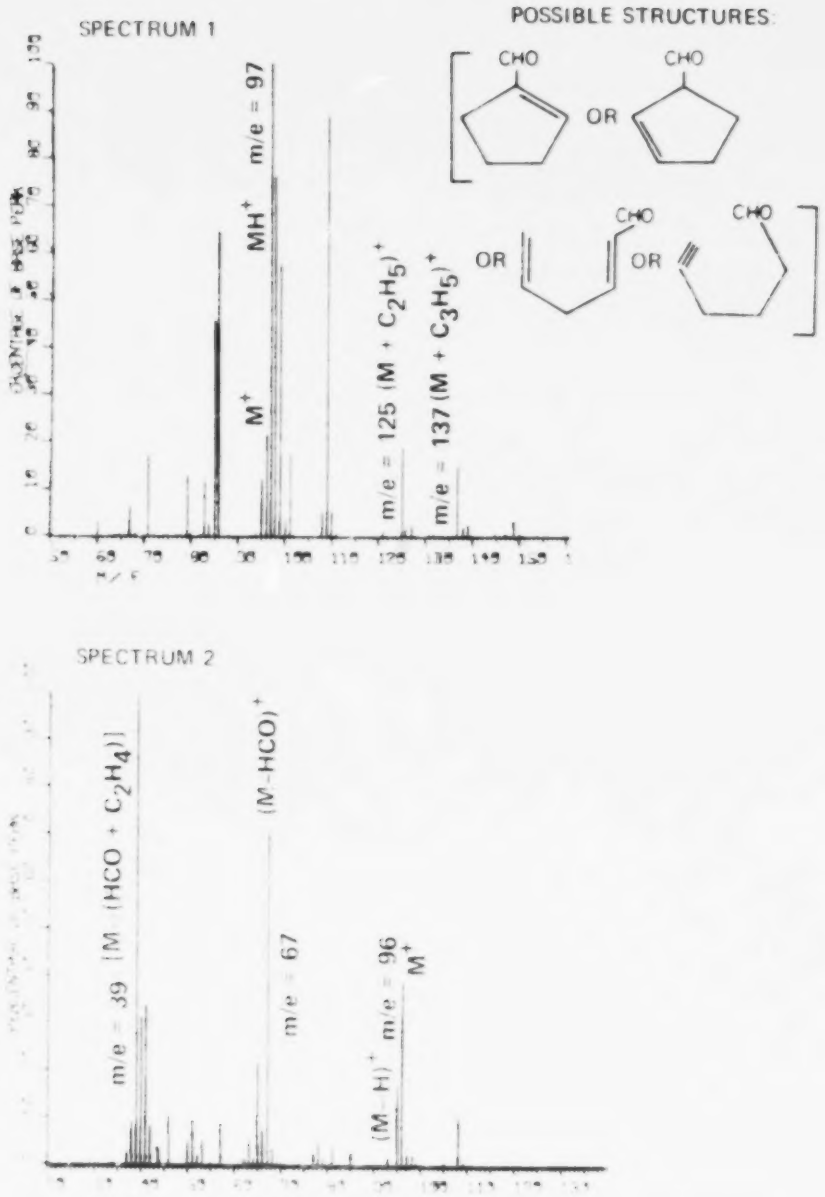
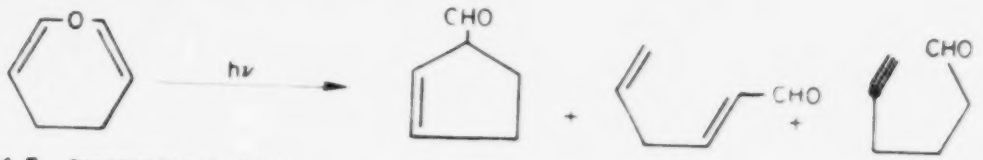


FIGURE 22. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION. CHEMICAL IONIZATION MASS SPECTRA FOR CHROMATOGRAPHIC PEAK A. SPECTRUM 1 BY METHANE CI-MS, SPECTRUM 2 BY HELIUM CI-MS.

(Refer to Chromatogram in Figure 21)

Additional unsaturated aldehydes might be accounted for on the basis of a reaction described by Cockcroft, et al.[49] Upon photoisomerization of 4,5-dihydroxyoxepin, the three products shown below were obtained. Reported electron impact spectra of all three isomers are similar to the helium chemical ionization spectrum for the cyclohexene aerosol product.



4,5—DIHYDROXYOXEPIN

Consider now the spectrum in Figure 23, corresponding to chromatographic peak B. The methane spectrum is consistent with a molecular weight of 112. Peaks are observed appropriate for protonated parent ion at m/e 113, and adduct ions at m/e 141 and 153 ($M + C_2H_5^+$ and $M + C_3H_5^+$). The helium spectrum shows fragments at m/e 97, 69, and 43, consistent with loss of CH_3, CH_3-CO, and CH_3-CO-CO from the parent ion. A possible structure consistent with the data is shown in the figure.

Finally, consider peak D, the mass spectrum for which is shown in Figure 24. In the methane spectra, peaks consistent with protonated parent and loss of water from protonated parent appear at m/e 99 and 81, respectively. In the helium spectrum, a peak at m/e 81 is similarly observed, as is a peak at m/e 31, consistent with the fragment $CH_2{=}OH^+$. The data suggest a primary alcohol of molecular weight 98. Additional fragmentation is rationalized in the figure and a possible structure is shown.

Structures presented in the last two figures suggest reactions of greater complexity than those considered up to this point. Moreover,

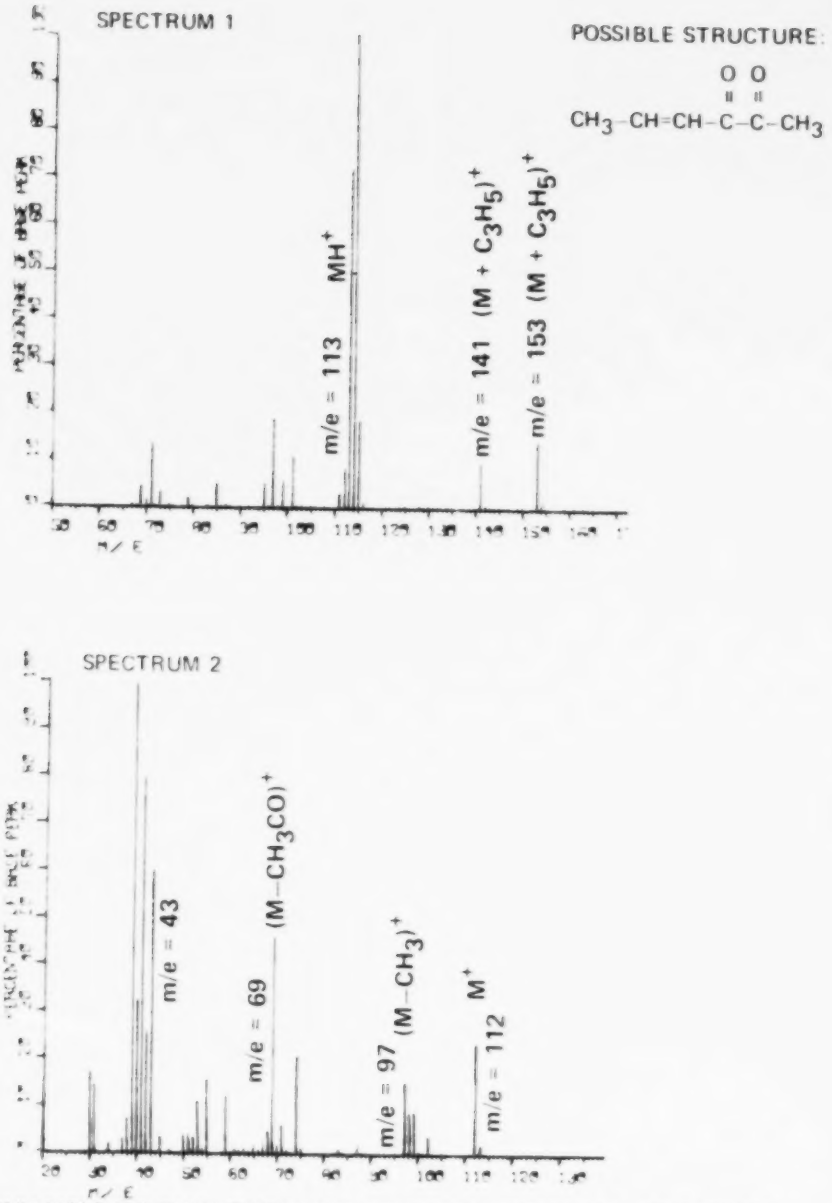
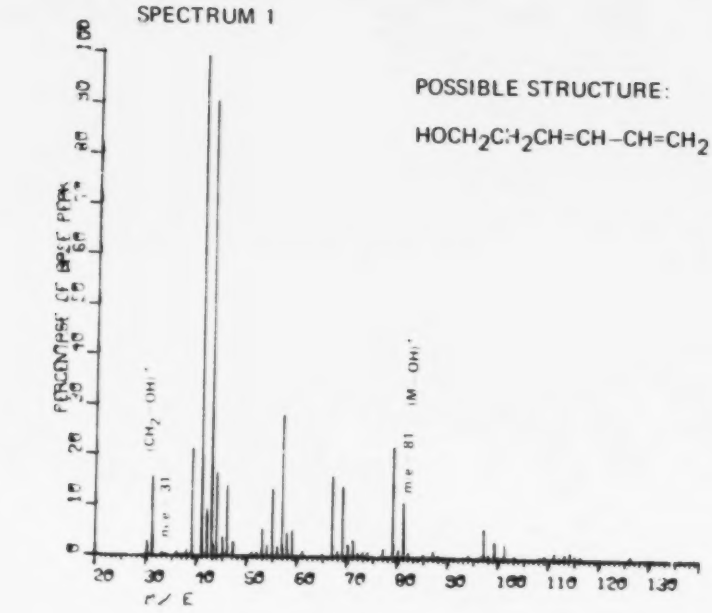


FIGURE 23. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION. CHEMICAL IONIZATION MASS SPECTRA FOR CHROMATOGRAPHIC PEAK B. SPECTRUM 1 BY METHANE CI-MS, SPECTRUM 2 BY HELIUM CI-MS.

(Refer to Chromatogram in Figure 21)



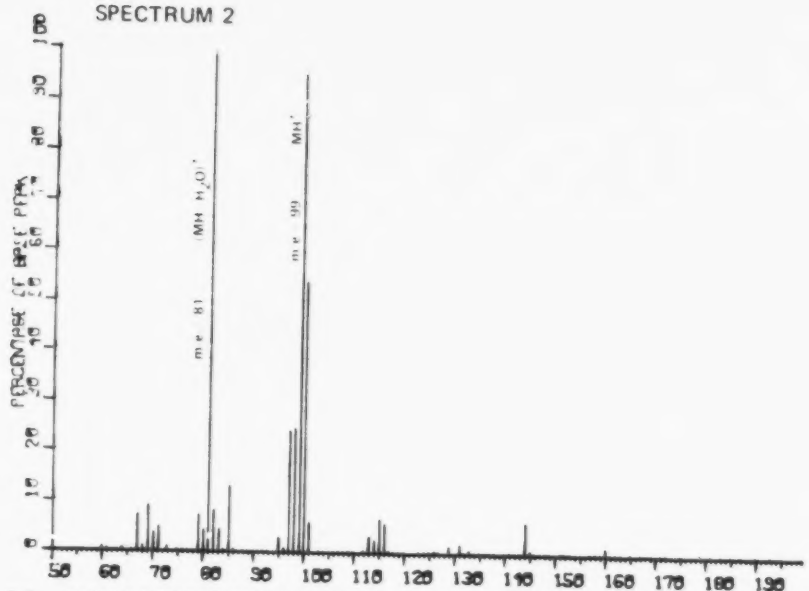


FIGURE 24. ANALYSIS OF CYCLOHEXENE AEROSOL, NEUTRAL FRACTION. CHEMICAL IONIZATION MASS SPECTRA FOR CHROMATOGRAPHIC PEAK D. SPECTRUM 1 BY METHANE CI-MS, SPECTRUM 2 BY HELIUM CI-MS.

(Refer to Chromatogram in Figure 21)

retention of unsaturation may appear surprising in view of the reaction conditions. It will be seen, however, that tentatively identified products in cyclohexene and α-pinene aerosols similarly retain such unsaturation.

Cyclohexene Aerosol Basic Fraction

The quantity of basic matter obtained upon fractionation of cyclohexene aerosol was extremely limited (~0.2 mg) and was insufficient for satisfactory analysis by GC-MS. Only in the case of α-pinene aerosol was sufficient material obtained in the basic fraction to permit such analysis. The general question concerning formation of nitrogen-bases during aerosol reactions is considered in the section dealing with the α-pinene aerosol.

ANALYSIS OF TOLUENE AEROSOL

Toluene Aerosol Acid Fraction

The water-insoluble acid fraction of toluene aerosol was isolated as previously described, and was treated with diazomethane to yield methyl esters and methyl-aryl ethers of the carboxylic acids and phenols. The derivatized product was then analyzed by gas chromatography and GC-MS. The reconstructed gas chromatogram is shown in Figure 25. Structures have tentatively been assigned for five of the prominent components and molecular weights have been assigned for two others. It is notable that four of the molecular weights shown have odd values, suggesting the presence of nitrogen.

The mass spectrum in Figure 26 corresponds to chromatographic peak B. The prominent peak at m/e 159 corresponds to the protonated parent ion. Strong adduct ions corresponding to $(M + C_2H_5^+)$ and $(M + C_3H_5^+)$ are observed at m/e 187 and 199 respectively. This clearly establishes the molecular weight as 158. Fragmentation corresponding to loss of $HCOOCH_3$ and loss of CH_3OH suggests the presence of carboxylic acid methyl ester. Loss of CO suggests the presence of an aldehyde,

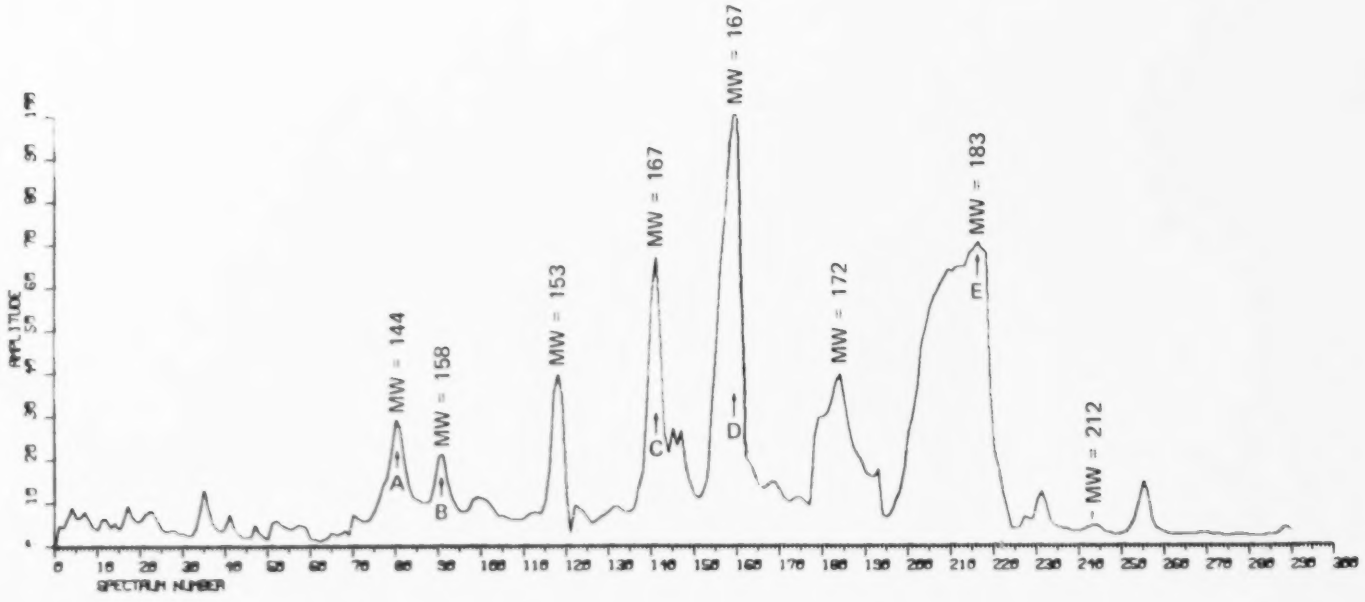


FIGURE 25. ANALYSIS OF TOLUENE AEROSOL, ACID FRACTION METHYL ESTERS/ETHERS. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

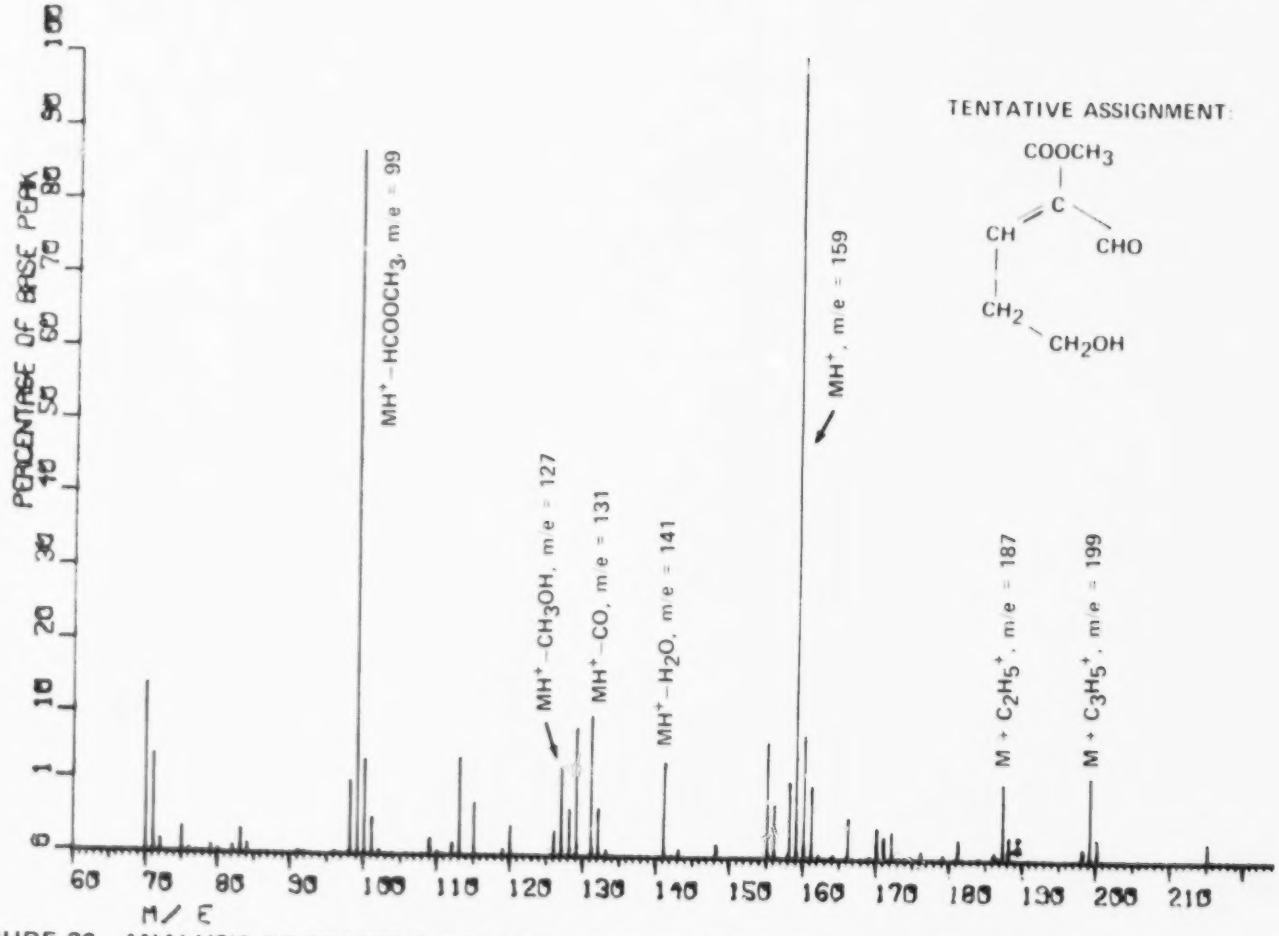


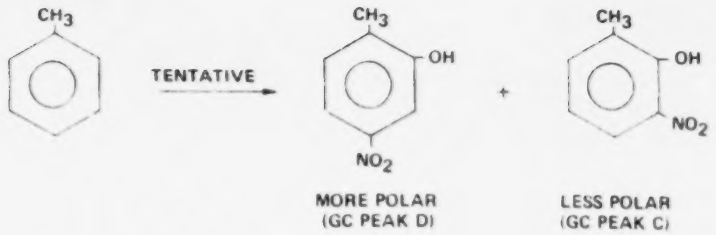
FIGURE 26. ANALYSIS OF TOLUENE AEROSOL, ACID FRACTION METHYL ESTERS/ETHERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK B. (Refer to Chromatogram in Figure 25.)

and loss of H_2O suggests the presence of alcohol. The structure shown in the figure is consistent with such fragmentation and with the molecular weight.

The mass spectrum in Figure 27 corresponds to chromatographic peak A. The prominent peak for protonated parent ion at m/e 145 and the adduct ions at m/e 173 and 185 indicate that the molecular weight is 144. Observed fragmentation is analogous to the previous case. The tentatively assigned structure is shown in the figure, and corresponds to the next lower homologue of the product considered in the case above.

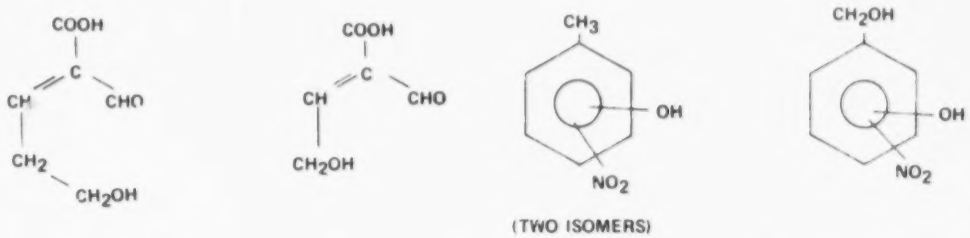
The mass spectrum corresponding to chromatographic peak C is shown in Figure 28. Peaks for the protonated parent ion and for the adduct ions indicate that this product has a molecular weight of 167. Since this is an odd number, the presence of nitrogen is indicated. Fragments corresponding to loss of NO and NO_2 confirm this and indicate that the product is probably a nitro compound. Fragmentation corresponding to loss of CH_4 may stem from the methyl ether group. Taking these and other factors into account, the structure shown in the figure is proposed. Substitution is not specified. It should be emphasized that the original product would be a phenol. Treatment with diazomethane leads to the formation of the methyl ether.

The mass spectrum in Figure 29 corresponds to peak D in the reconstructed gas chromatogram. Almost all of the comments concerning the last product apply to the one considered here, with the exception that this spectrum does not show a fragment corresponding to loss of NO. Nevertheless, the evidence strongly suggests the proposed structure. Thus, it appears that two isomeric nitro-cresols are formed. Since chromatographic component D has a longer retention time than component C we can speculate that substitution of component D renders it more polar than C. Some possibilities are shown below.



Consider next, the mass spectrum of chromatographic component E, shown in Figure 30. The spectrum shows a strong protonated parent ion and adduct ions indicating that the molecular weight is 183. Again, the presence of nitrogen is indicated. There are peaks consistent with loss of NO, NO_2, and H_2O. The strong peak for loss of H_2O is especially suggestive of an alcohol. Consistent with these data the substituted benzyl alcohol is proposed.

The structures below summarize our findings to date concerning the acid fraction of toluene aerosol. The formation of such homologous degradation products parallels our findings concerning the aerosol reactions of cyclohexene. In addition we see that both the methyl group and the benzene ring of toluene appear to undergo attack independently. It is noteworthy that the most abundant components of this fraction appear to be nitrogen-containing compounds and that nitration of an aromatic ring appears to be taking place during aerosol formation.



(TWO ISOMERS)

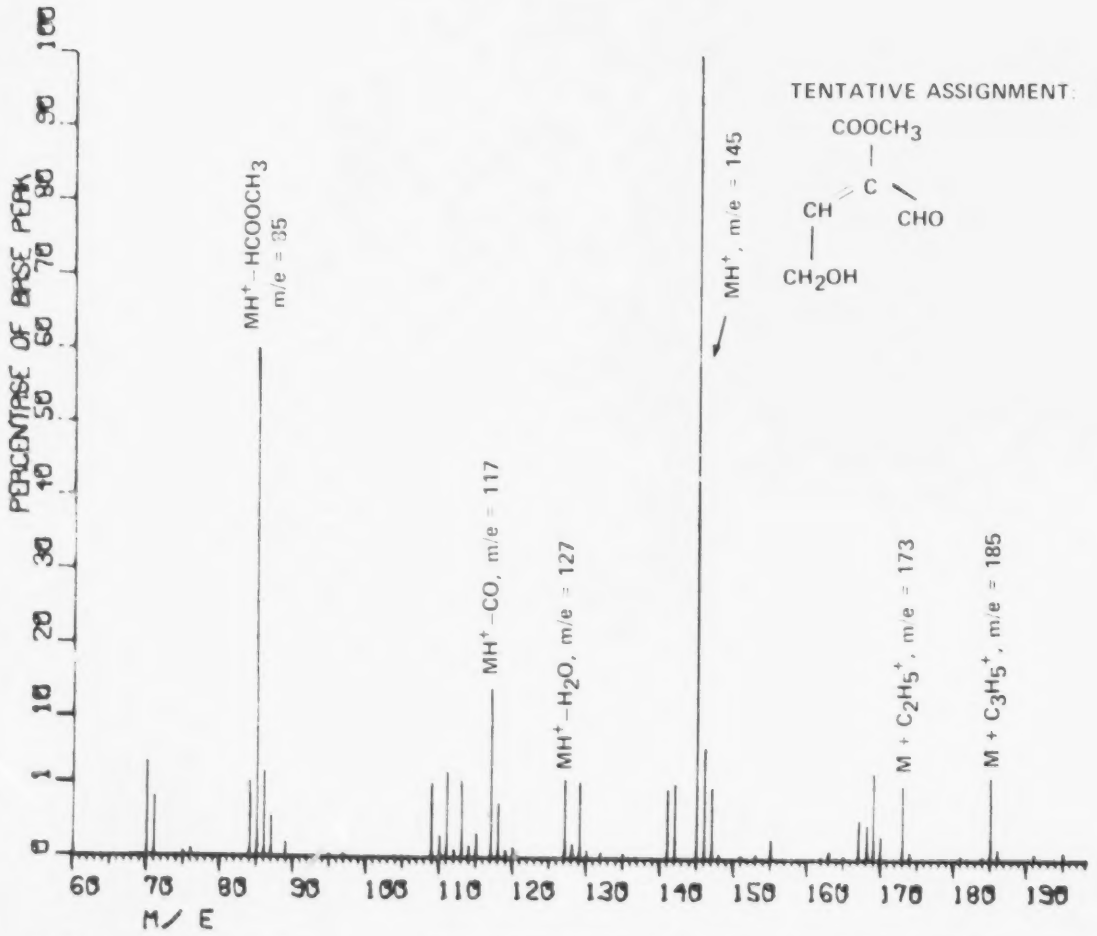


FIGURE 27. ANALYSIS OF TOLUENE AEROSOL, ACID FRACTION METHYL ESTERS/ETHER. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK A.
(Refer to Chromatogram in Figure 25)

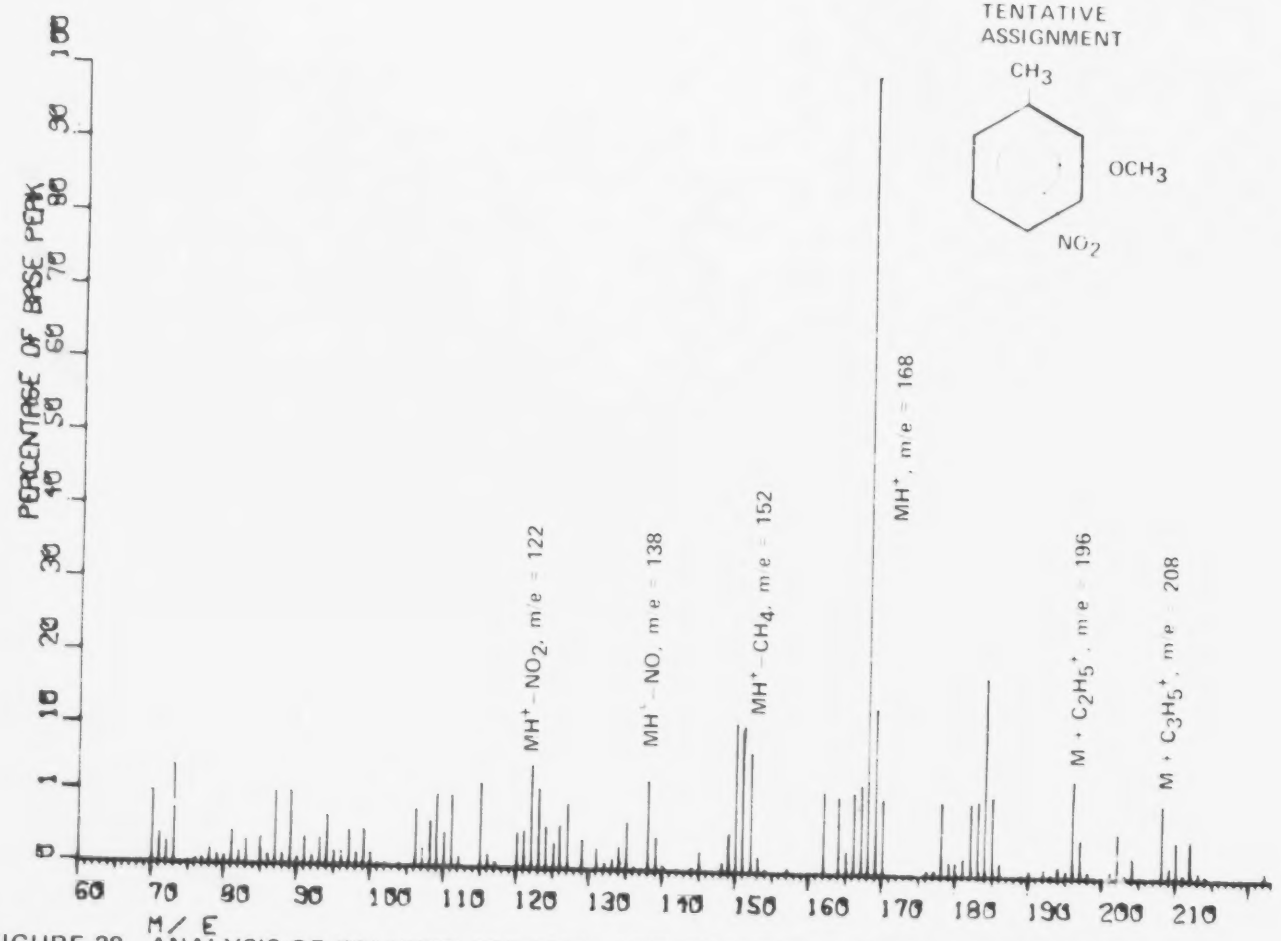


FIGURE 28. ANALYSIS OF TOLUENE AEROSOL, ACID FRACTION METHYL ESTERS/ETHERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK C.
(Refer to Chromatogram in Figure 25)

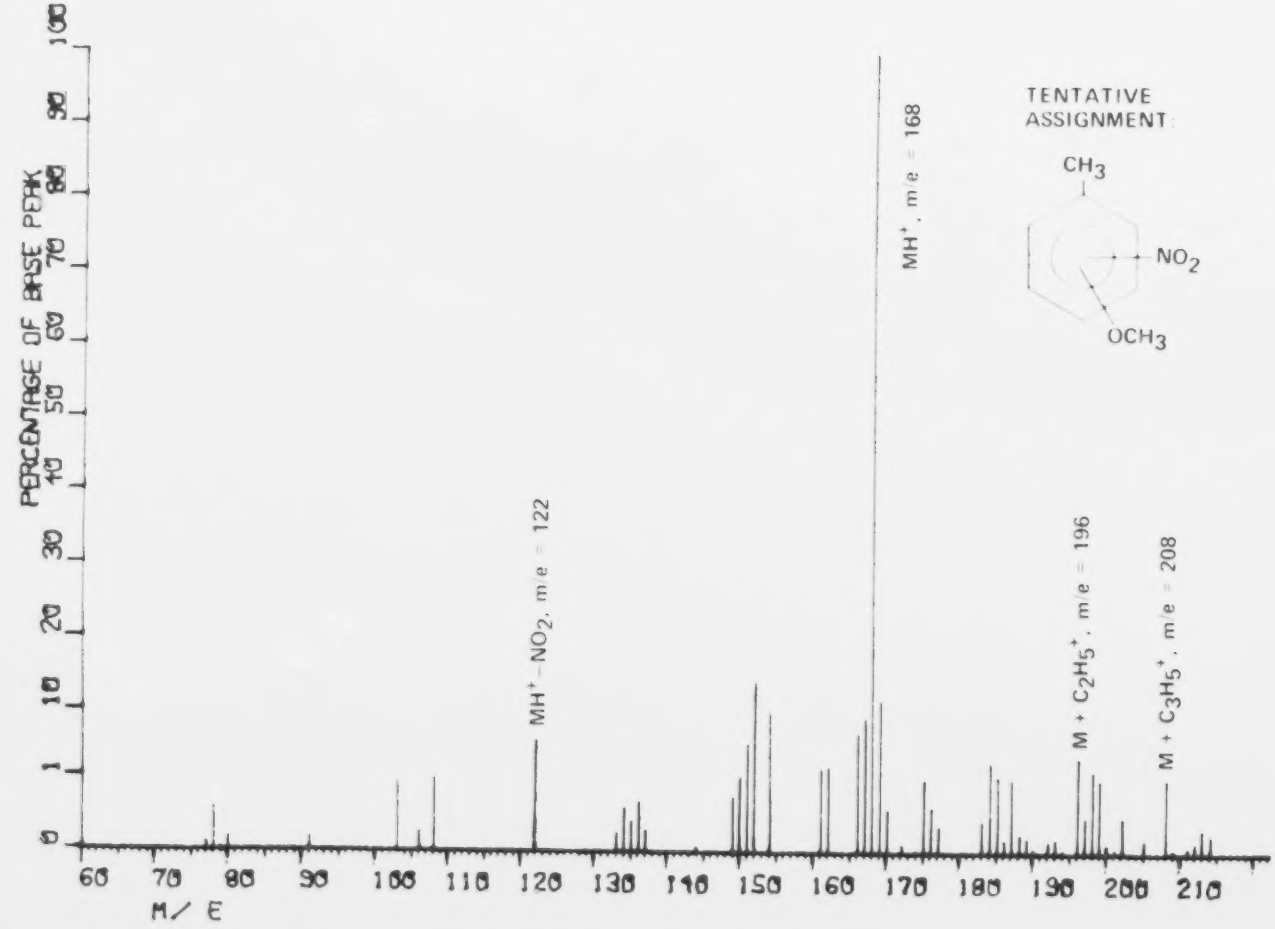


FIGURE 29. ANALYSIS OF TOLUENE AEROSOL, ACID FRACTION METHYL ESTERS/ETHERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK D

(Refer to Chromatogram in Figure 25)

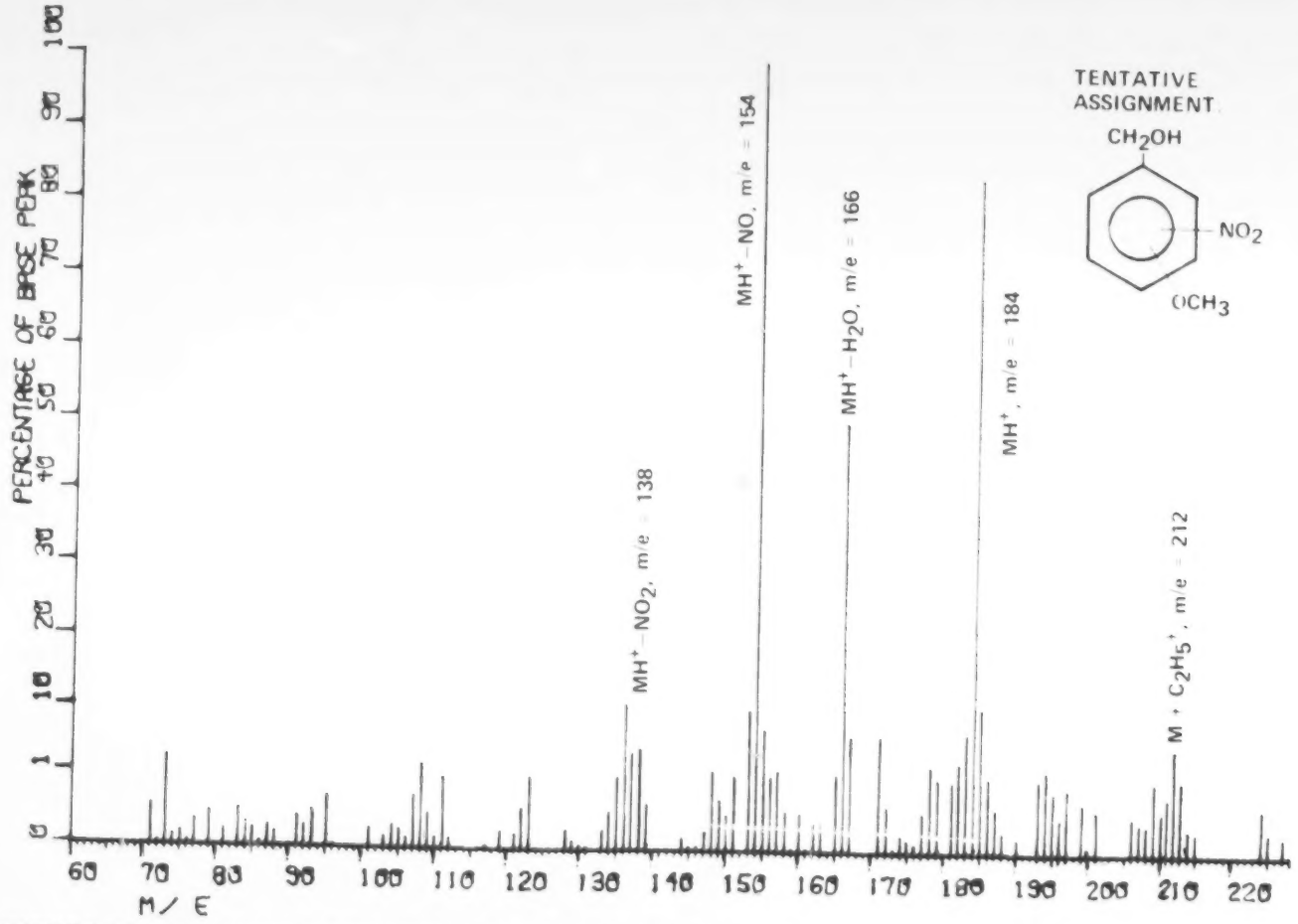


FIGURE 30. ANALYSIS OF TOLUENE AEROSOL, ACID FRACTION METHYL ESTERS/ETHERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK E.

(Refer to Chromatogram in Figure 25)

Toluene Aerosol Neutral Fraction

The water-insoluble neutral fraction of toluene aerosol was isolated as described previously, and was analyzed by gas chromatography and GC-MS. The reconstructed gas chromatogram is shown in Figure 31. Note that tentative assignments have been made for four major peaks and molecular weights have been assigned to six others. In this fraction one major and one minor peak have odd molecular weights, suggesting the presence of nitrogen in these compounds.

The mass spectrum in Figure 32 corresponds to chromatographic peak B. Peaks assigned to protonated parent ions and adduct ions suggest a product of molecular weight 112. Loss of CH_4 may arise possibly from an intact methyl group, while loss of H_2CO suggests the presence of aldehyde. Consistent with these data a tentative structure is shown in the figure.

The mass spectrum corresponding to chromatographic peak F is shown in Figure 33. The spectrum is practically devoid of fragmentation, but a strong protonated parent peak and reasonably prominent adduct ions strongly suggest a molecular weight of 126. Very minor fragments are evident which correspond to loss of H_2O and CH_4. This spectrum is particularly ambiguous. A possible structure is shown in the figure.

The mass spectrum in Figure 34 corresponds to chromatographic peak A. The spectrum is wholly devoid of significant fragmentation; peaks at m/e 97 and 99 are considered spurious background in view of the unrealistic M-12 and M-14 values. However, the molecular weight can be determined with some confidence as 110 in view of the adduct ions for $(M + C_2H_5^+)$ and $(M + C_3H_5^+)$. The proposed structures shown in the figure, however, are extremely resonance stabilized and could reasonably account for resistance to fragmentation under conditions of chemical ionization mass spectrometry (methane).

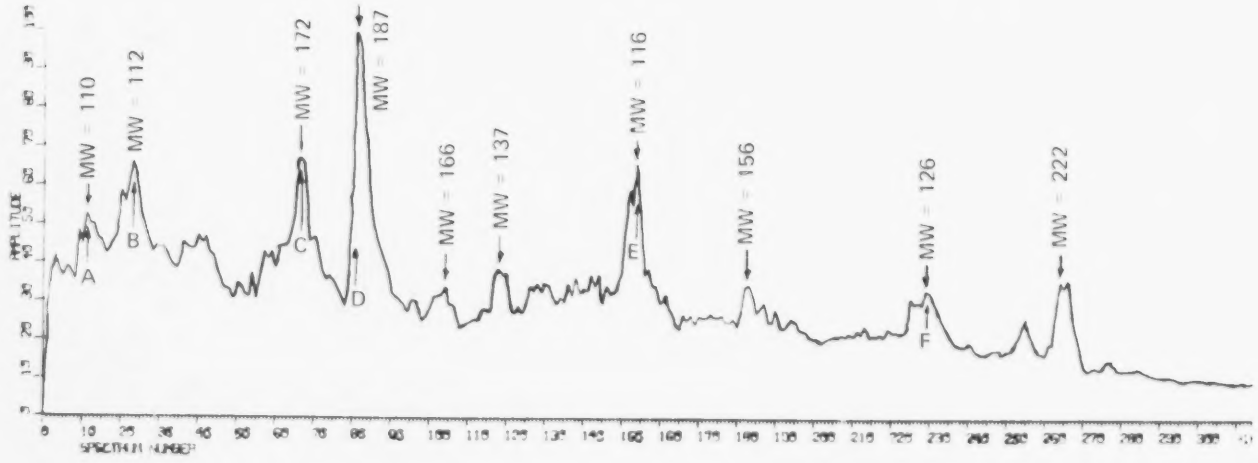


FIGURE 31. ANALYSIS OF TOLUENE AEROSOL, NEUTRAL FRACTION. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

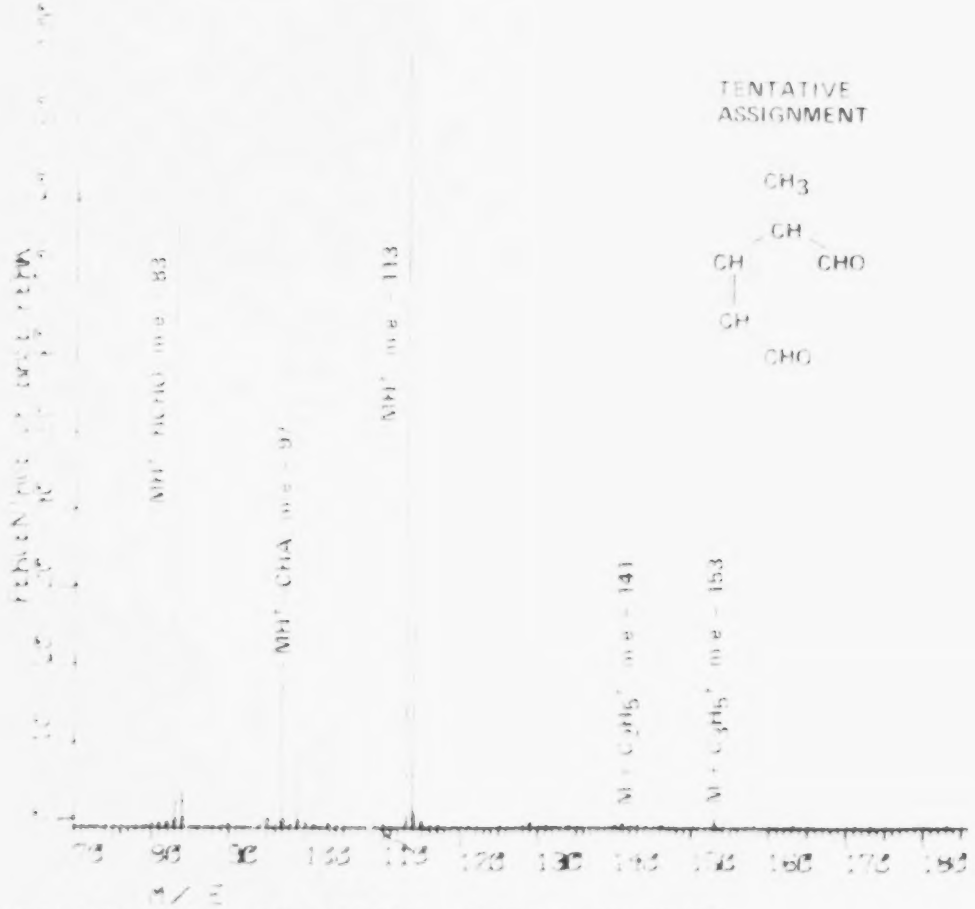


FIGURE 32. ANALYSIS OF TOLUENE AEROSOL NEUTRAL FRACTION CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK B.

Refer to Chromatogram in Figure 31.

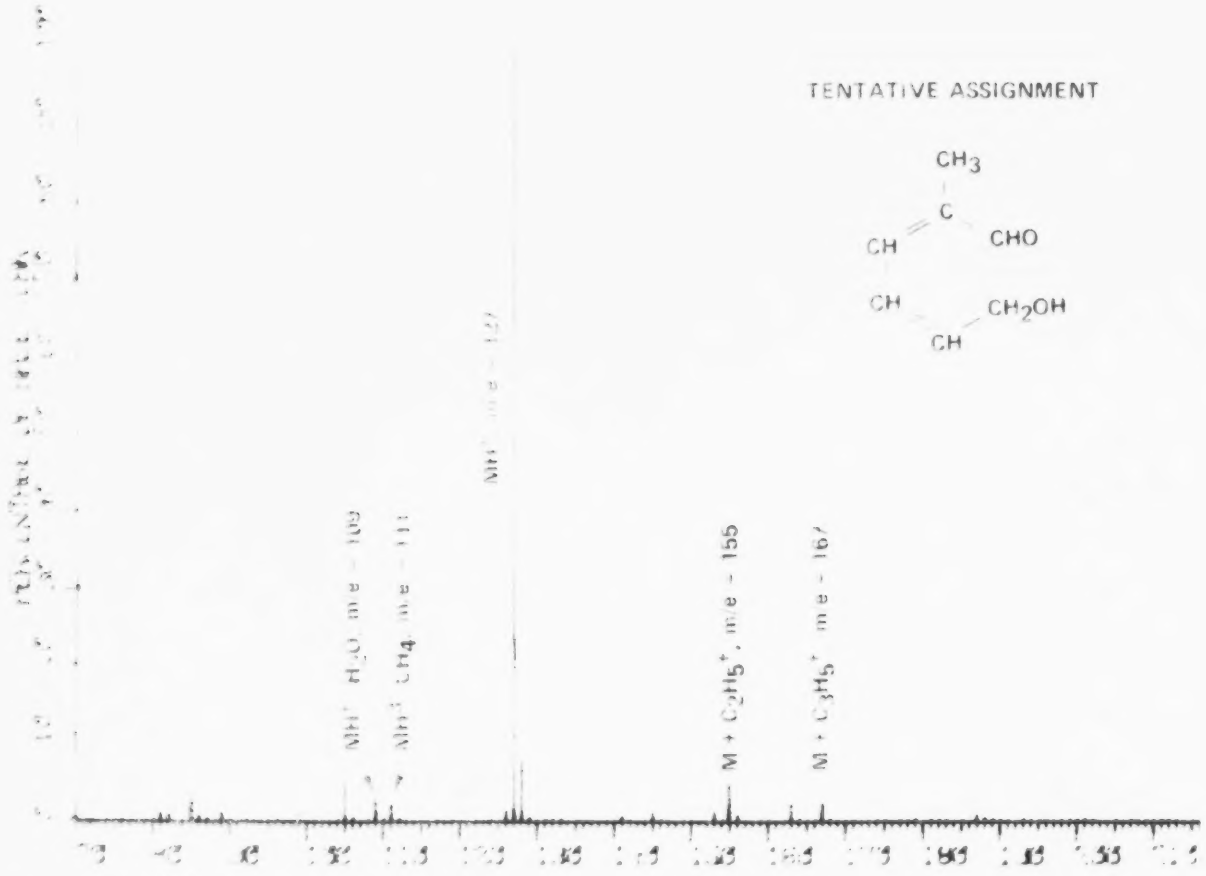
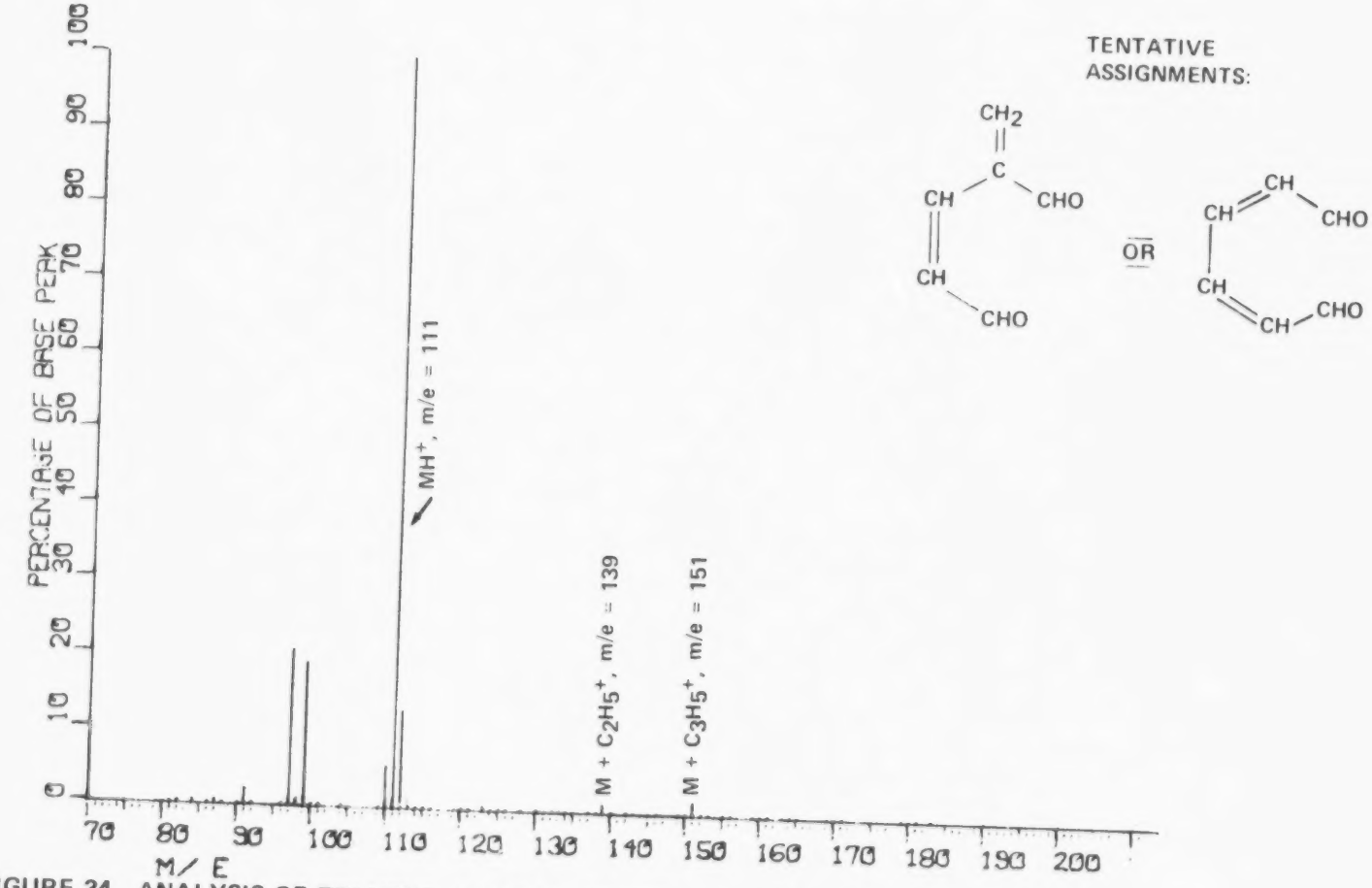


FIGURE 33. ANALYSIS OF TOLUENE AEROSOL, NEUTRAL FRACTION. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK F

(Refer to Chromatogram in Figure 31)

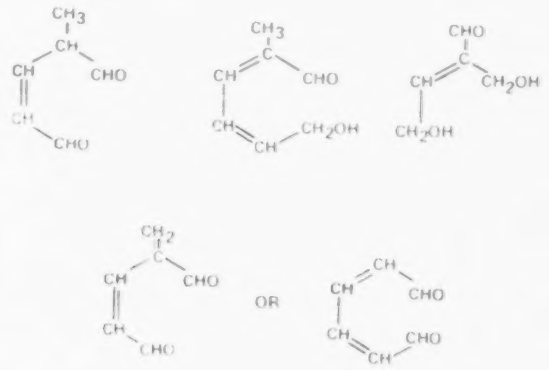


TENTATIVE ASSIGNMENTS:

FIGURE 34. ANALYSIS OF TOLUENE AEROSOL, NEUTRAL FRACTION. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK F. (Refer to Chromatogram in Figure 31)

Finally, consider the mass spectrum in Figure 35, corresponding to chromatographic component E. The spectrum is rather weak, but significant adduct ions permit determination of the most probable molecular weight as 116. The prominent peak corresponding to loss of H_2O strongly suggests the presence of alcohol functionality. Consistent with these data, and with fragmentation of apparently related products of toluene, a possible structure is shown in the figure.

The structures shown below summarize the finding to date concerning the water-insoluble neutral fraction of toluene aerosol. As in the previously considered product mixtures, we again observe sequential oxidative degradation to give a series of related oxidation products.



ANALYSIS OF α-PINENE AEROSOL

In studying the α-pinene aerosol, extensive reference has been made to the literature concerning reactions of this compound. This was especially helpful during analyses of the neutral fraction, where mass spectral data indicated the presence of many isomeric products. Salient aspects of the literature survey are summarized under the headings below. Detailed reviews of the chemistry of α-pinene and other terpines have been prepared by Simonsen[50] and Templeton[51].

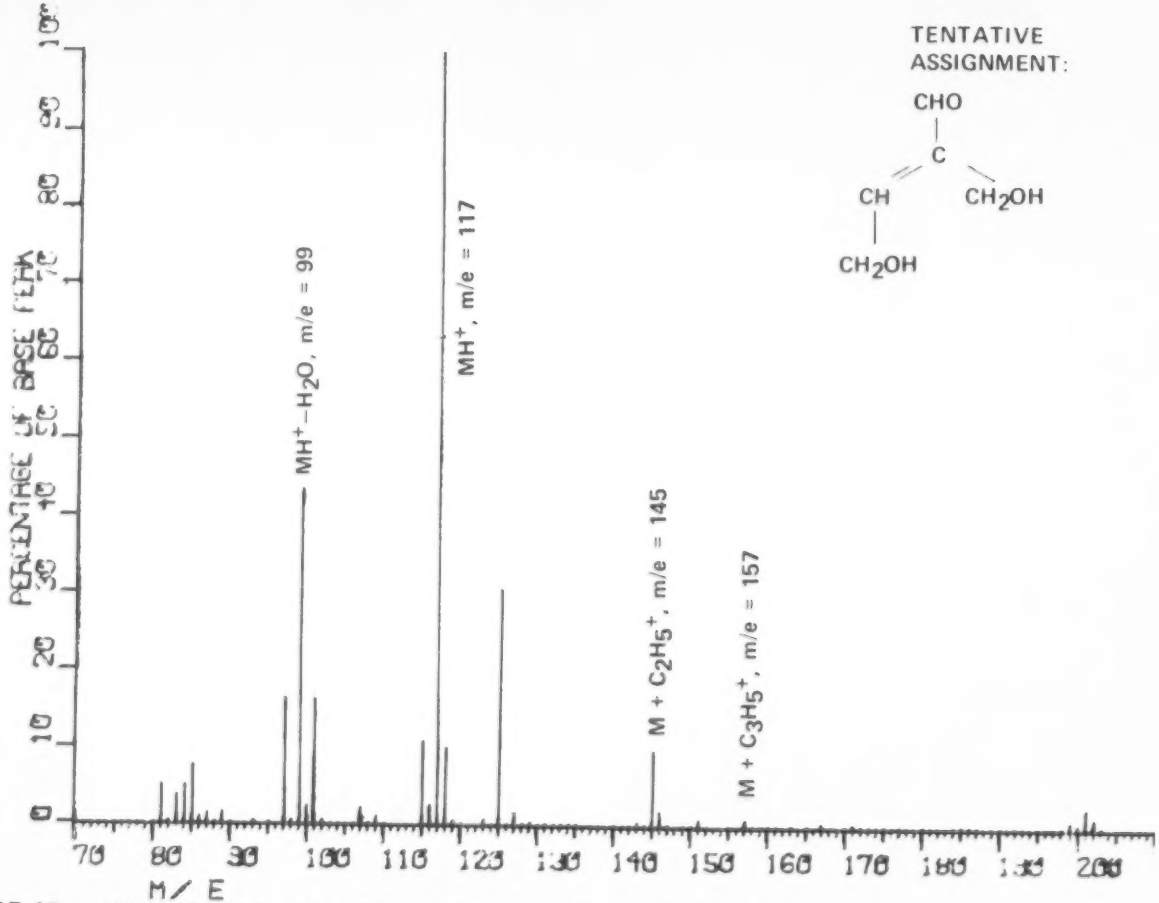
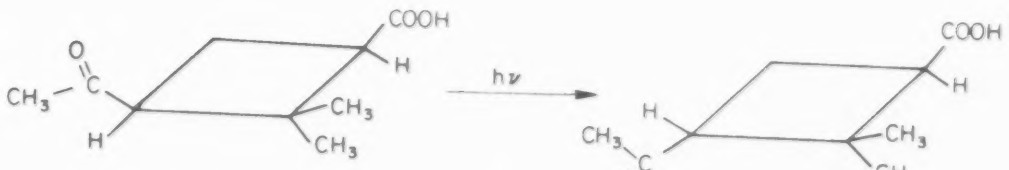


FIGURE 35. ANALYSIS OF TOLUENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK E.
(Refer to Chromatogram in Figure 31)

α-Pinene Acid Fraction

The α-pinene acid fraction was isolated as described previously, and was treated with diazomethane to form methyl esters of the carboxylic acids. The material was then analyzed by gas chromatography and GC-MS. Figure 36 shows the reconstructed gas chromatogram. The indicated chromatographic component whose mass spectrum is shown in Figure 37 has been unequivocally identified as methyl-cis-pinonate by comparison with an authentic sample of methyl-cis-pinonate. The mass spectrum of the latter compound is shown in Figure 38. The mass spectral fragmentation pattern for this compound is rationalized in Table 4.

A second analysis of the sample by GC-MS verified the presence of pinonic acid. The results indicated, in addition, that trans-pinonic acid may be present along with the more abundant cis isomer. As indicated below, interconversion of the isomers in the presence of ultraviolet irradiation can be postulated. Tentative identification of the chromatographic peaks corresponding to the isomeric pinonic acid esters is indicated on the reconstructed gas chromatogram in Figure 39.



CIS-PINONIC ACID

TRANS-PINONIC ACID

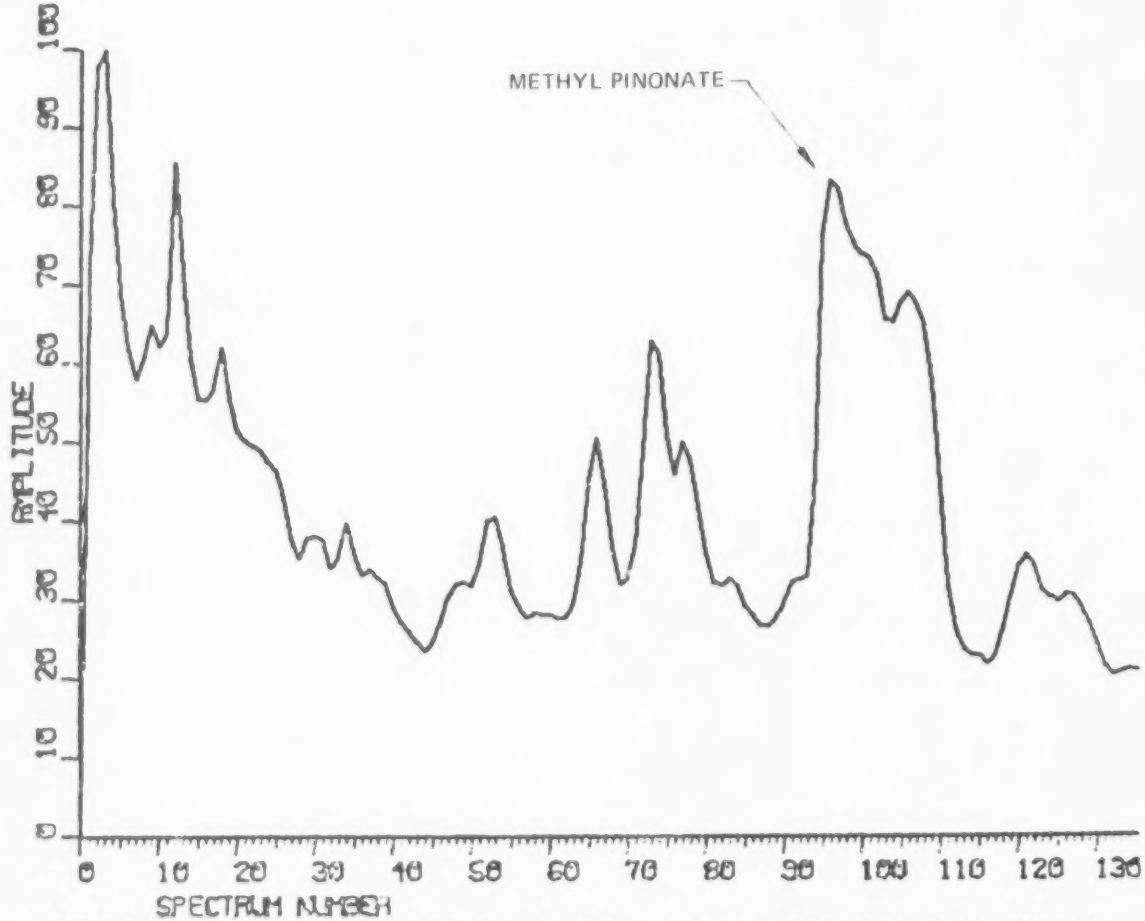


FIGURE 36. ANALYSIS OF α-PINENE AEROSOL, ACID FRACTION METHYL ESTERS. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

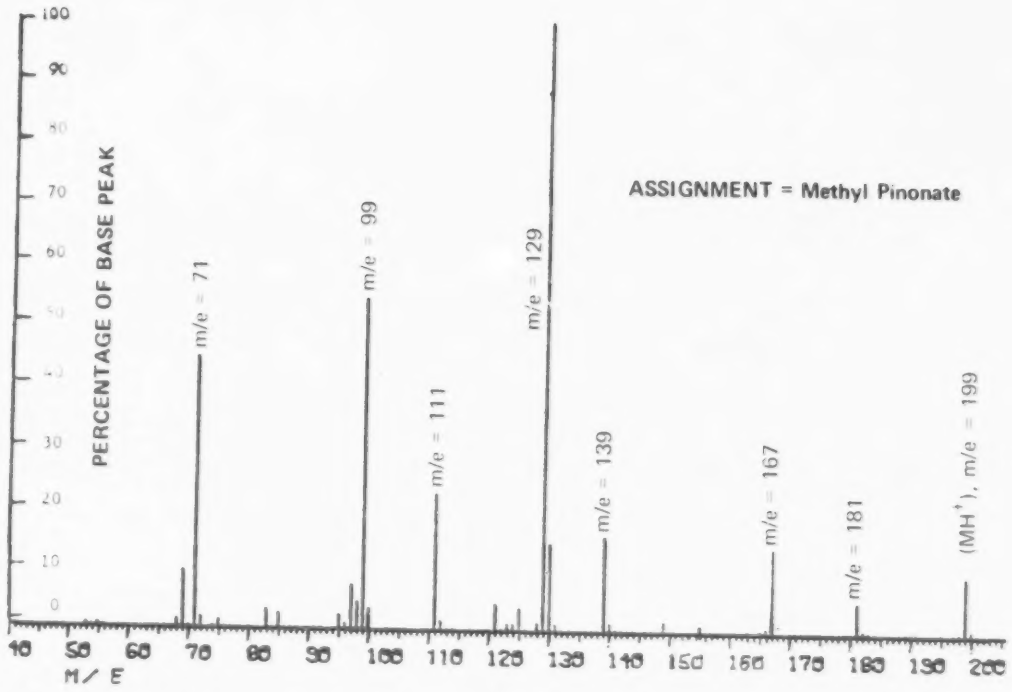


FIGURE 37. ANALYSIS OF α-PINENE AEROSOL, ACID FRACTION METHYL ESTERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) CORRESPONDING TO METHYL PINONATE.

(Refer to Chromatogram in Figure 36)

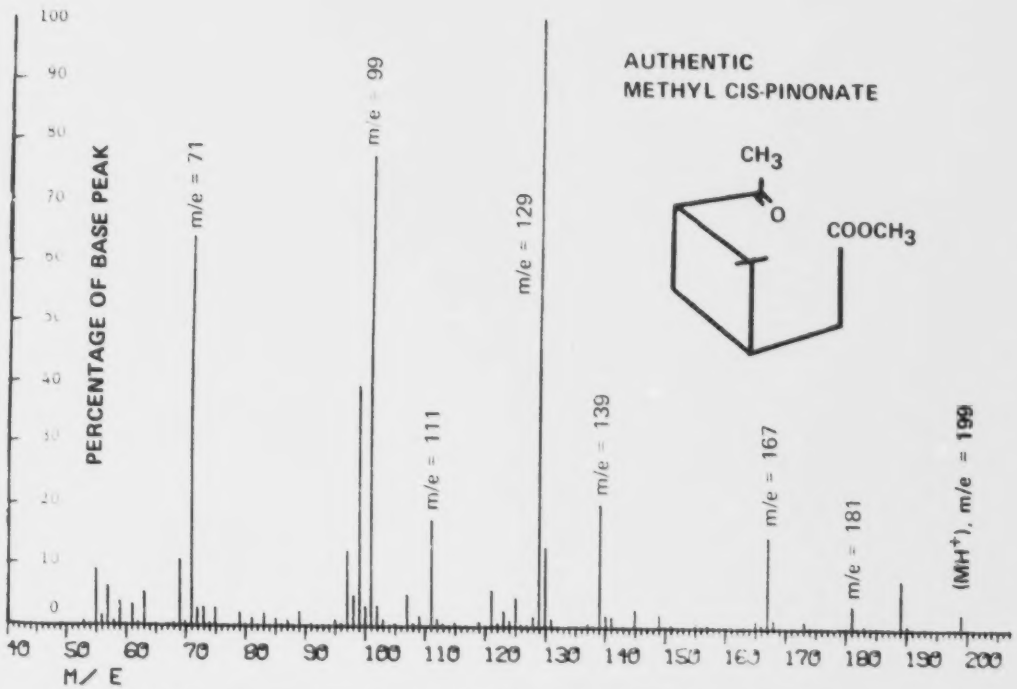
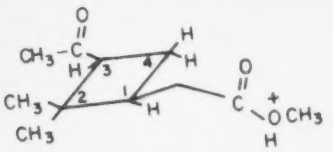


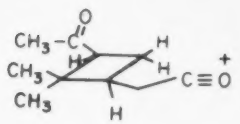
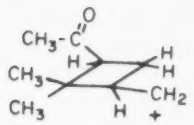
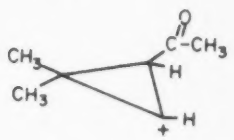
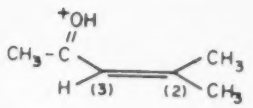
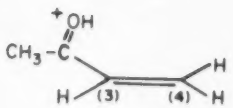
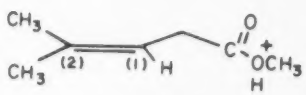
FIGURE 38. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) OF AUTHENTIC METHYL CIS-PINONATE

TABLE 4. RATIONALIZED FRAGMENTATION OF AUTHENTIC METHYL PINONATE UNDER CONDITIONS OF CHEMICAL IONIZATION MASS SPECTROMETRY (METHANE)



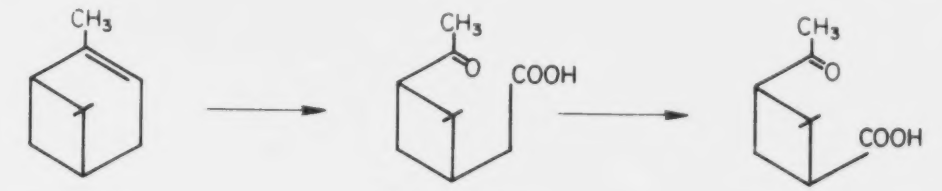
Protonated parent-ion of methyl pinonate, $(MH)^+$, m/e = 199

Fragmentation of Parent-Ion

Process	Fragment	m/e
Loss of $H_2O(MH^+-18)$	— — — — —	181
Loss of $CH_3OH(MH^+-32)$		167
Loss of $HCOOCH_3(MH^+-60)$		139
Transannular cleavage		111
Transannular cleavage		99
Transannular cleavage		71
Transannular cleavage		129

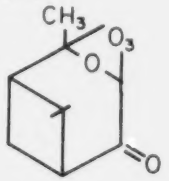
Tentative identification of a secondary reaction product of α-pinene has been made. The compound corresponds to peak A of the reconstructed gas chromatogram in Figure 39. Its mass spectrum is shown in Figure 40. The compound is tentatively identified as the homologous acid resulting from oxidative decarboxylation of pinonic acid, that is, pinononic acid. Its mass spectral fragmentation pattern is rationalized in Table 5. The compound is referred to as pinononic acid in accordance with nomenclature of Simonson [52]. In previous reports it has been referred to using the derived name "nor-pinonic acid".

In summary the data indicate that under the simulated atmospheric conditions α-pinene undergoes oxidative cleavage to pinonic acid. The pinonic acid produced may then be oxidatively decarboxylated (tentative) to the next lower homologous acid.

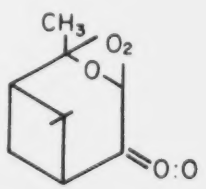


α-PINENE PINONIC ACID PINONONIC ACID

Formation of pinononic acid may also occur without intermediate formation of pinonic acid. In a study of vapor-phase ozonation of α-pinene by Spencer, et al [53], an intermediate ozonide, $C_{10}H_{16}O_5$, was hydrolyzed to give pinononic acid directly. The authors speculate that the intermediate was either verbenone oxoozonide or verbenone peroxide ozonide



VERBENONE OXOOZONIDE



VERBENONE PEROXIDE OZONIDE

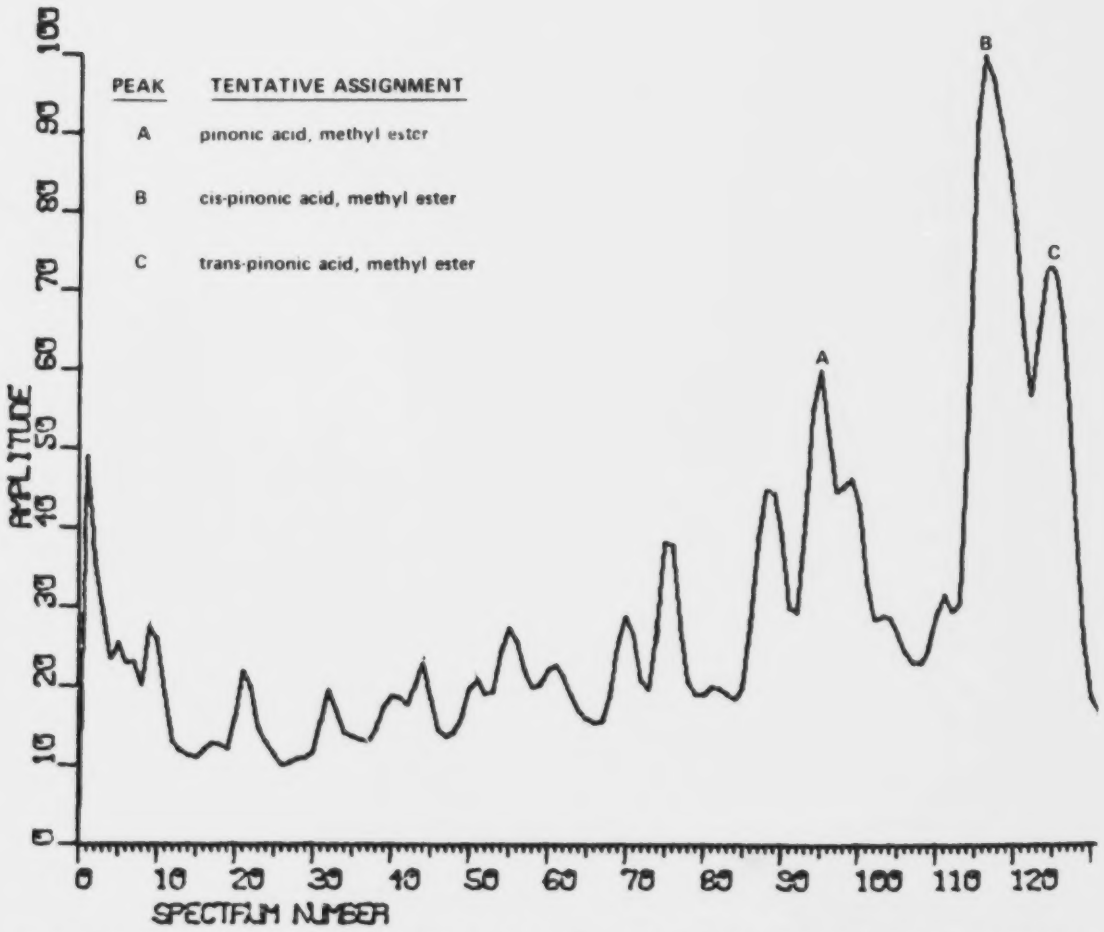


FIGURE 39. ANALYSIS OF α-PINENE AEROSOL, ACID FRACTION METHYL ESTERS. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

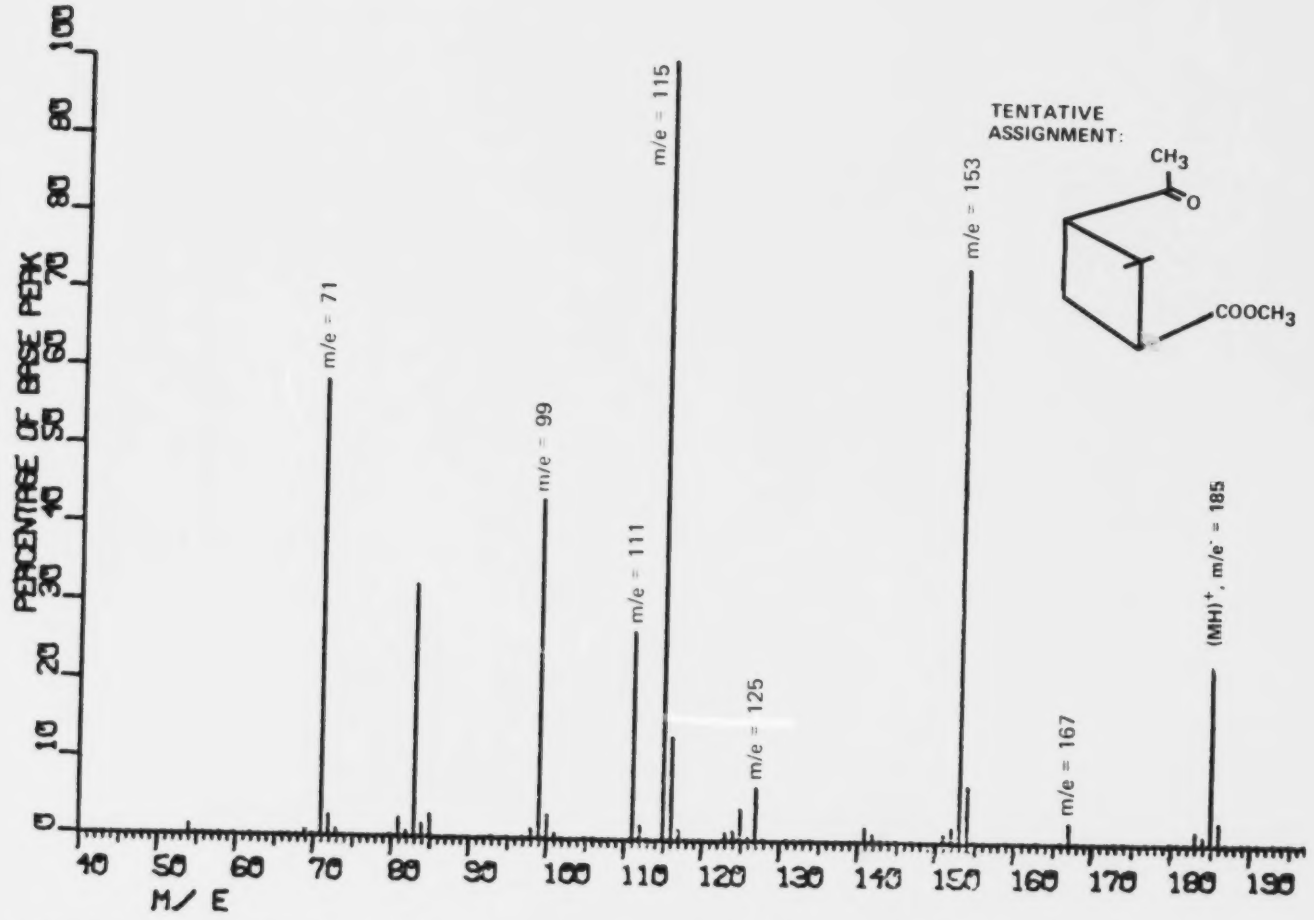
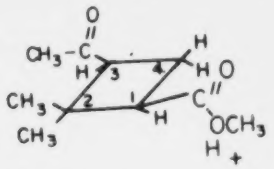


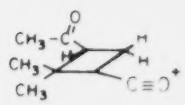
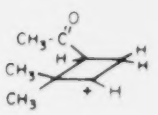
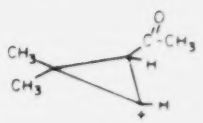
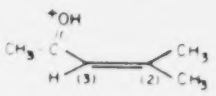
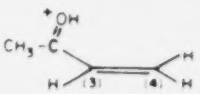
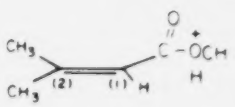
FIGURE 40. ANALYSIS OF α-PINENE AEROSOL, ACID FRACTION METHYL ESTERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK A. (Refer to Chromatogram in Figure 39)

TABLE 5. RATIONALIZED FRAGMENTATION OF TENTATIVELY IDENTIFIED METHYL PINONATE UNDER CONDITIONS OF CHEMICAL IONIZATION MASS SPECTROMETRY (METHANE)



Protonated parent-ion of methyl "nor-pinonate", $(MH)^+$, m/e = 185.

Fragmentation of Parent-Ion

Process	Fragment	m/e
Loss of $H_2O(MH^+-18)$	— — —	167
Loss of $CH_3OH(MH^+-32)$		153
Loss of $HCOOCH_3(MH^+-60)$		125
Transannular cleavage		111
Transannular cleavage		99
Transannular cleavage		71
Transannular cleavage		115

In view of the identification of pinonic acid in model aerosol, this compound was sought in rural air particulate matter collected* in the Blue Ridge Mountains. The sampling site was located in the Pisgah National Forest, about 30 miles northeast of Ashville, North Carolina. There was extensive conifer and hardwood forest cover.

The organic acid fraction of the air particulate matter was isolated and treated with diazomethane, and the methyl esters were analyzed by GC-MS. The reconstructed gas chromatogram is shown in Figure 41. The mass spectrum shown in Figure 42 identifies the indicated chromatographic peak as pinonic acid, by comparison with the mass spectrum of an authentic sample (Figure 37).

The presence of pinonic acid was similarly sought in urban air particulate collected in New York City (lower Manhattan). No detectable concentration of the acid was observed.

α-Pinene Neutral Fraction

The water-insoluble neutral fraction of α-pinene aerosol products was isolated as previously described, and was analyzed by gas chromatography and GC-MS. The reconstructed gas chromatogram is shown in Figure 43. Molecular weights tentatively determined from the mass spectra are shown on the chromatogram. The data indicate that a number of isomeric reaction products have been obtained. In order to aid identification of these products various authentic terpenoids were obtained for use as reference compounds. Selection of reference compounds was based on a study of known reactions of α-pinene.

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* Sampling and analysis of atmospheric particulate matter was conducted under support of the previously cited program, "Haze Formation: Its Nature and Origin"[34].

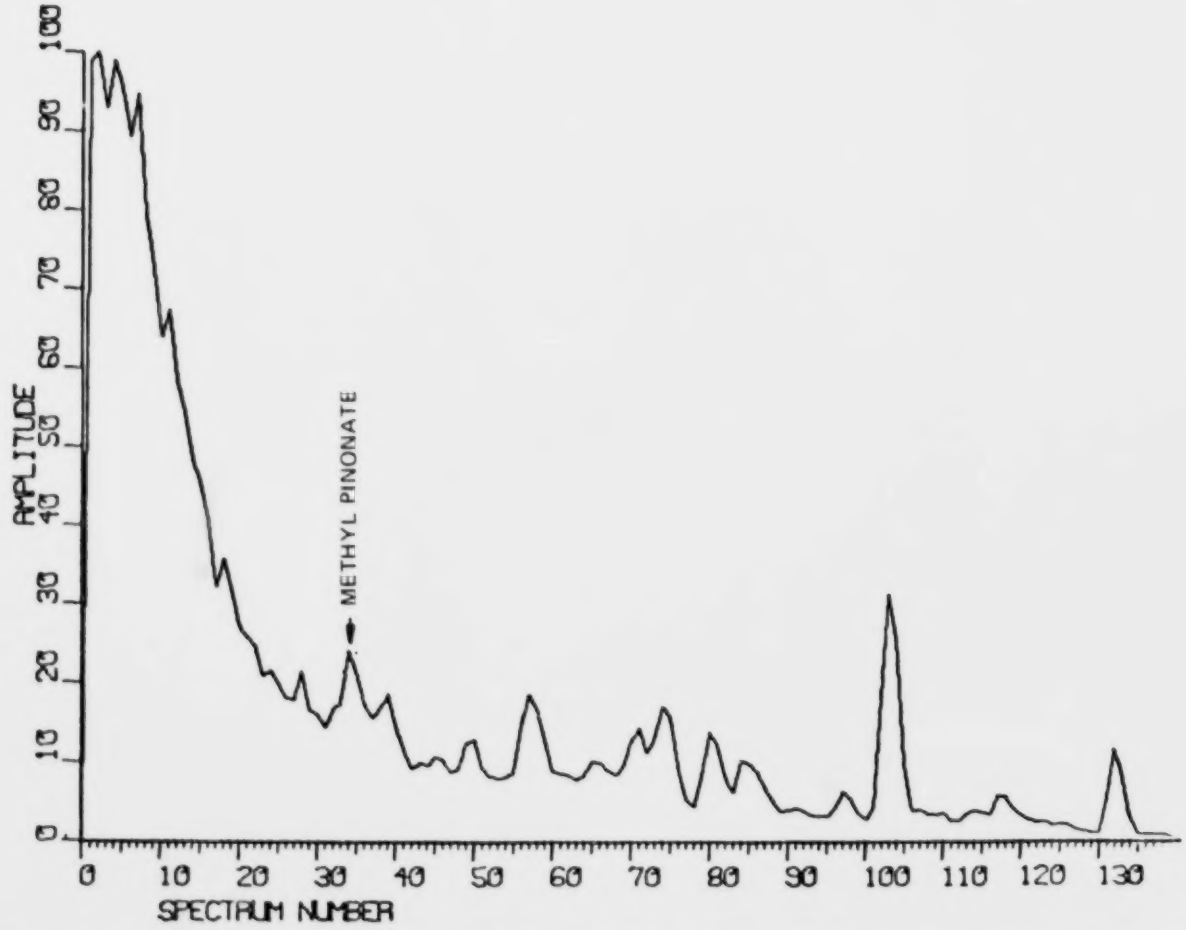


FIGURE 41. ANALYSIS OF BLUE RIDGE MOUNTAIN AEROSOL, ACID FRACTION METHYL ESTERS. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

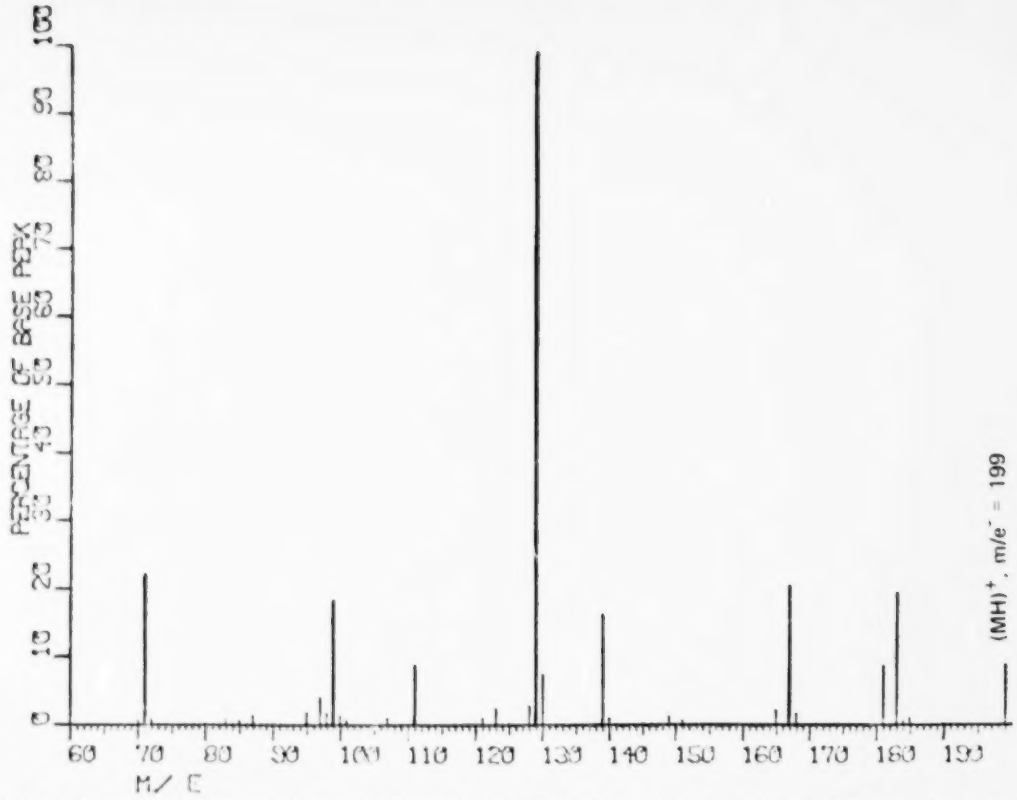


FIGURE 42. ANALYSIS OF BLUE RIDGE MOUNTAIN AEROSOL, ACID FRACTION METHYL ESTERS. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) CORRESPONDING TO METHYL PINONATE

(Refer to Chromatogram in Figure 41)

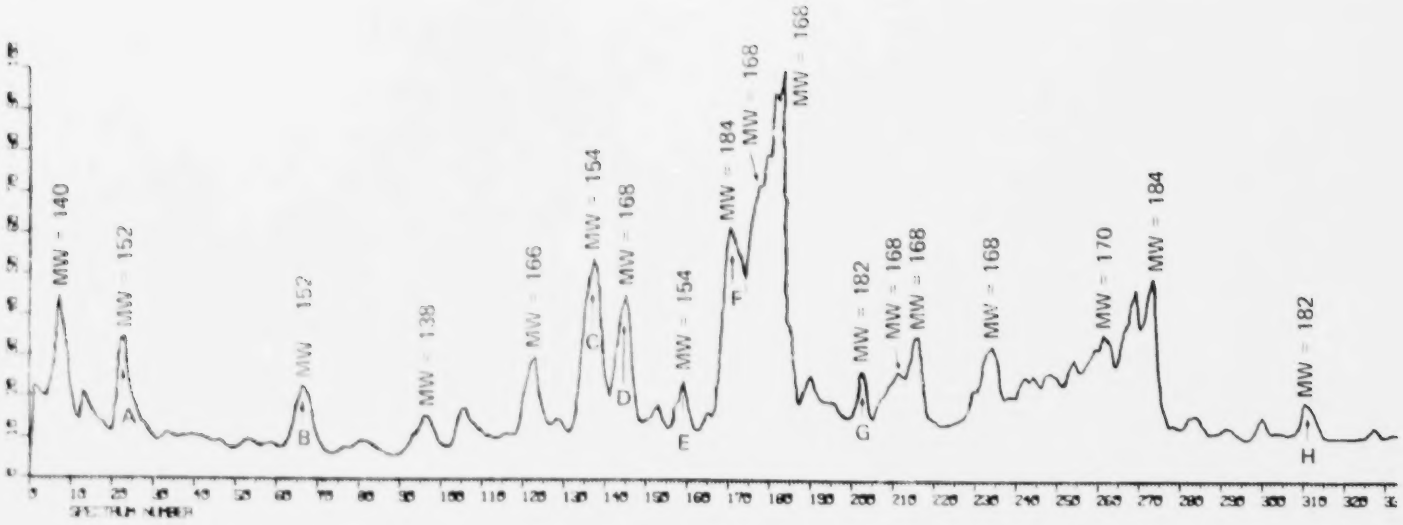
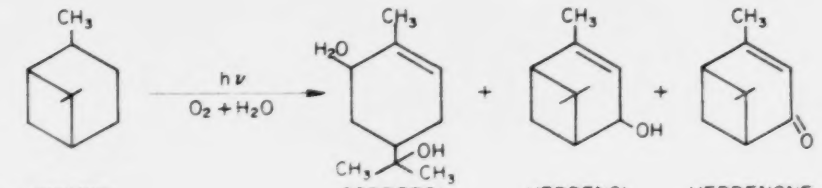
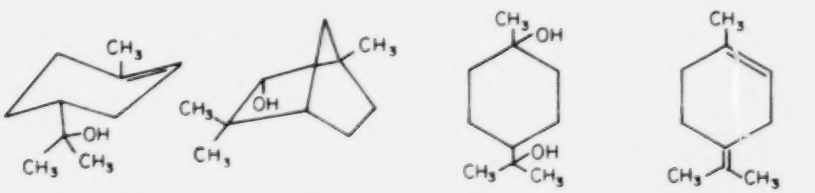


FIGURE 43. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

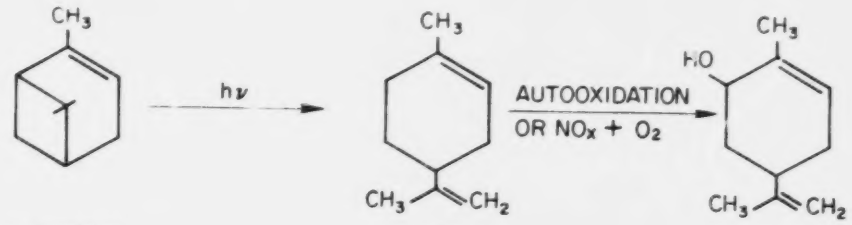
Studies Based on Known Reactions of α-Pinene - Simonsen[54] and Templeton[55] review a number of early studies concerning the "autooxidation" of α-pinene. When α-pinene is exposed to sunlight in the presence of moisture and air, it is converted principally to sobrerol; some verbenol and verbenone are also formed.



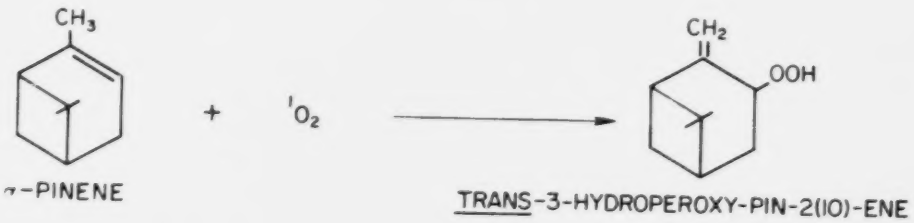
Like other bicyclic monoterpenoids, α-pinene undergoes facile rearrangement of the bicyclic skeleton[56]. Under aqueous acid conditions rearrangement and hydration occur[57]. In the presence of benzene sulfonic acid, α-terpineol is formed. In the presence of mixed acetic and sulfuric acids, α-fenchyl alcohol is obtained. Further acid catalyzed hydration of α-pinene yields 1,8-terpin. In the reverse direction, the acid catalyzed dehydration of α-terpineol yields terpinolene[58].



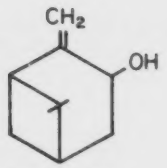
A study by Mayer, et al[47], indicates that when α-pinene is simply irradiated using a Pyrex filter, several products are obtained (low yields). One of the most abundant is d-limonene. Limonene itself can react in the presence of nitrogen oxides, or by "autooxidation" to form carveol.



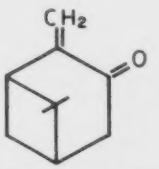
Jefford reports that reaction of photogenerated singlet oxygen with α-pinene results in greater than 99 percent yield of trans-3-hydroperoxy-pin-2(10)-ene.



A reaction of this type could presumably occur in aerosol containing a suitable sensitizer. The hydroperoxide may undergo unimolecular or bimolecular reaction to yield the hydroxy or carbonyl compounds, pinocarveol and pinocarvone. (Although neither pinocarveol nor pinocarvone could be obtained for use as reference standards, note that in the chromatogram, Figure 43, two peaks have molecular weights corresponding to that of pinocarveol, 152).

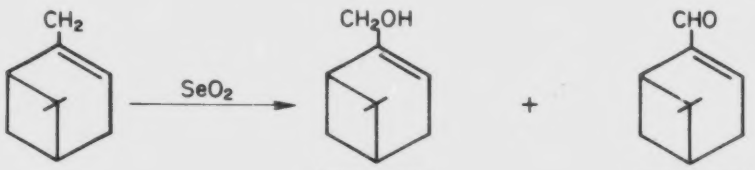


PINOCARVEOL



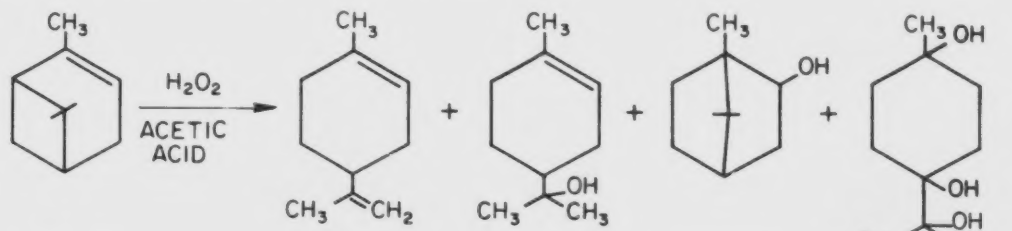
PINOCARVONE

Dupont and Zacharowitz[59] showed that oxidation of α-pinene in the presence of selenium dioxide yields myrtenol and myrtenal. This is significant with respect to atmospheric chemistry because both selenium dioxide and singlet oxygen lead to allylic oxidation. Both compounds below were obtained for use as reference standards.



MYRTENOL MYRTENAL

Henderson and Sutherland[60] observed that hydrogen peroxide treatment of α-pinene in acetic acid yields principally limonene, α-terpineol, borneol, and p-methane-1,4,8-triol.

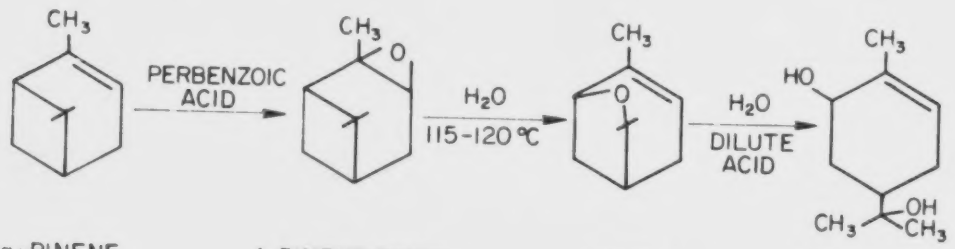


α-PINENE LIMONENE α-TERPINEOL BORNEOL p-MENTHANE-1,4,8-TRIOL

Although the above is a liquid-phase reaction in acetic acid, it should be pointed out that hydrogen peroxide has been observed in the atmosphere and in model systems[61]. It was observed in irradiated mixtures of hydrocarbon/NO_x and in the urban atmosphere during periods of photochemical smog formation.

Finally, oxidation of α-pinene by perbenzoic acid has been described.[62]

The reaction is of interest in that perbenzoic acid oxidation might be expected to yield products similar to those formed in the presence of peroxyacyl nitrates. The perbenzoic acid oxidation was shown to yield pinene oxide. Treatment of pinene oxide with water at 115-112 C yields pinol. Hydration in the presence of dilute acid leads to ring fission and formation of sobrerol.



α-PINENE 1-PINENE OXIDE PINOL SOBREROL

Of the α-pinene reaction products described above, those listed below were obtained for use as reference standards. Commercial samples of sobrerol, pinol, and pinene oxide could not be obtained.

(1) d-limonene
(2) terpinolene
(3) fenchyl alcohol
(4) fenchone
(5) l-borneol
(6) α-terpineol
(7) cis-terpin (hydrate)
(8) trans-verbenol
(9) l-carveol
(10) myrtenol
(11) myrtenal

Mixtures of these authentic compounds were analyzed by GS-MS. The reconstructed gas chromatograms are shown in Figure 44. Mass spectra are shown in Figures 45-50. In the paragraphs below, the comparison standards have been grouped by molecular weight, and α-pinene neutral products of appropriate molecular weight are compared in turn with the reference spectra. A reconstructed gas chromatogram showing the

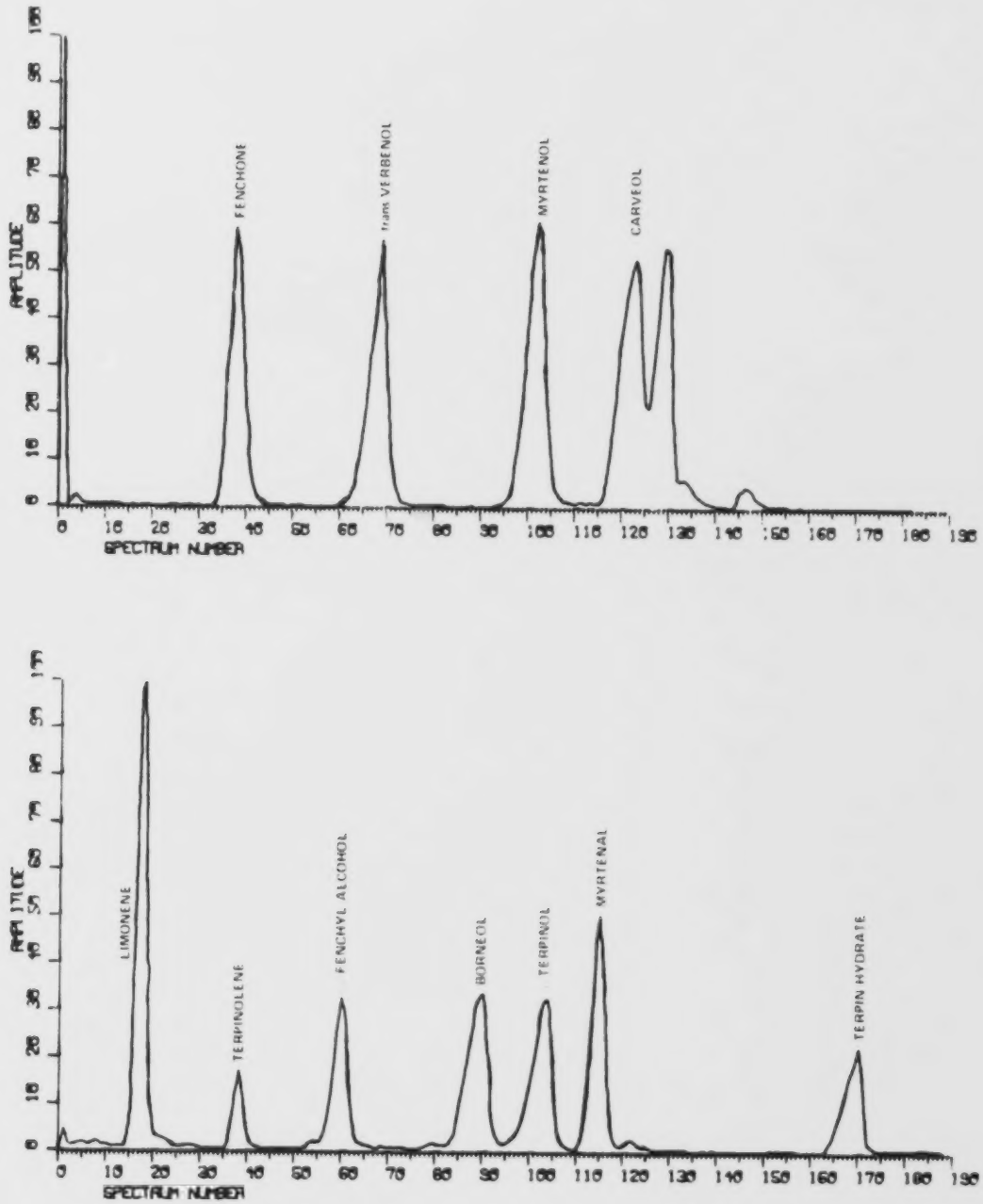


FIGURE 44. RECONSTRUCTED GAS CHROMATOGRAMS OF AUTHENTIC TERPENOIDS.

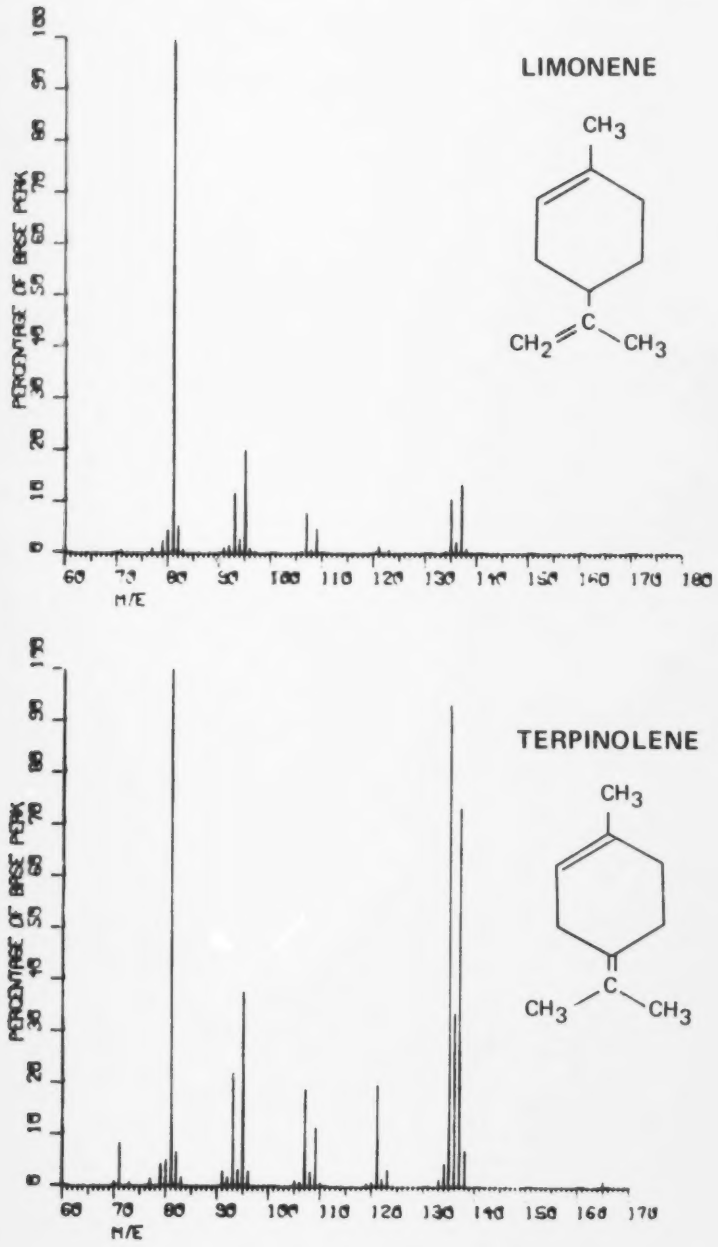


FIGURE 45. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC LIMONENE AND TERPINOLENE.

(Refer to Chromatograms in Figure 44)

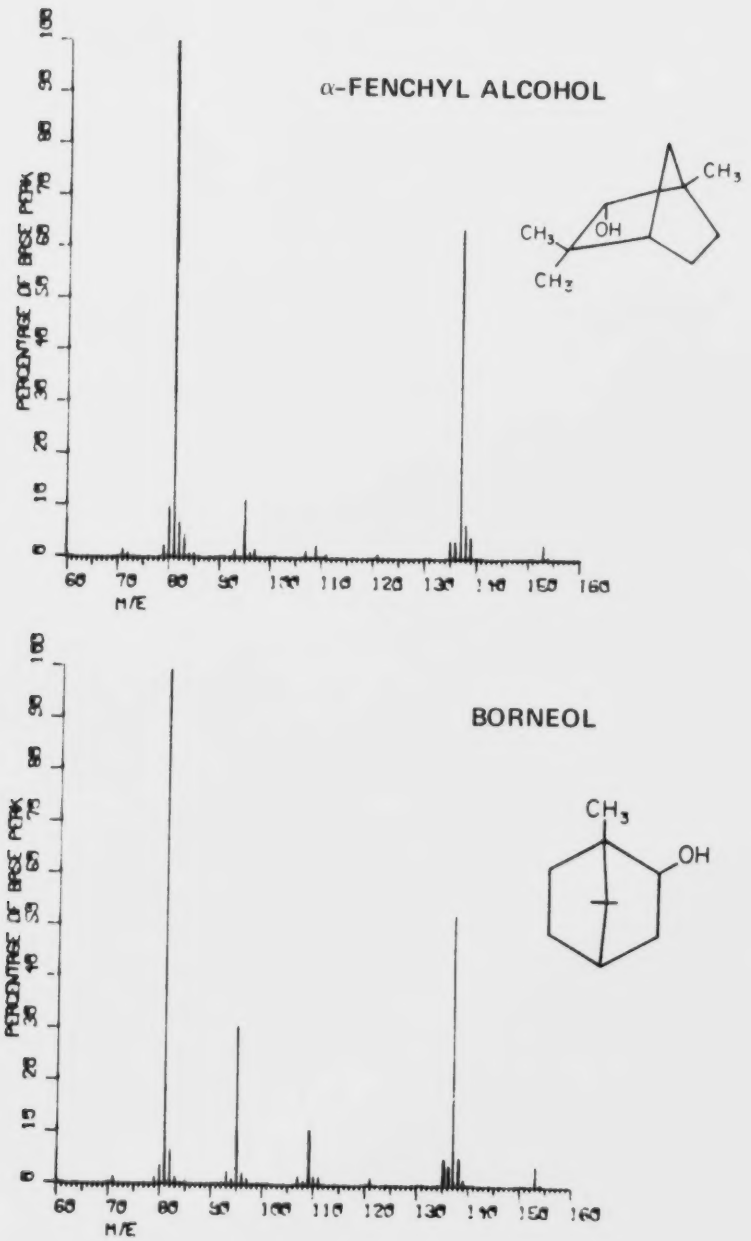


FIGURE 46. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC α-FENCHYL ALCOHOL AND BORNEOL.

(Refer to Chromatograms in Figure 44)

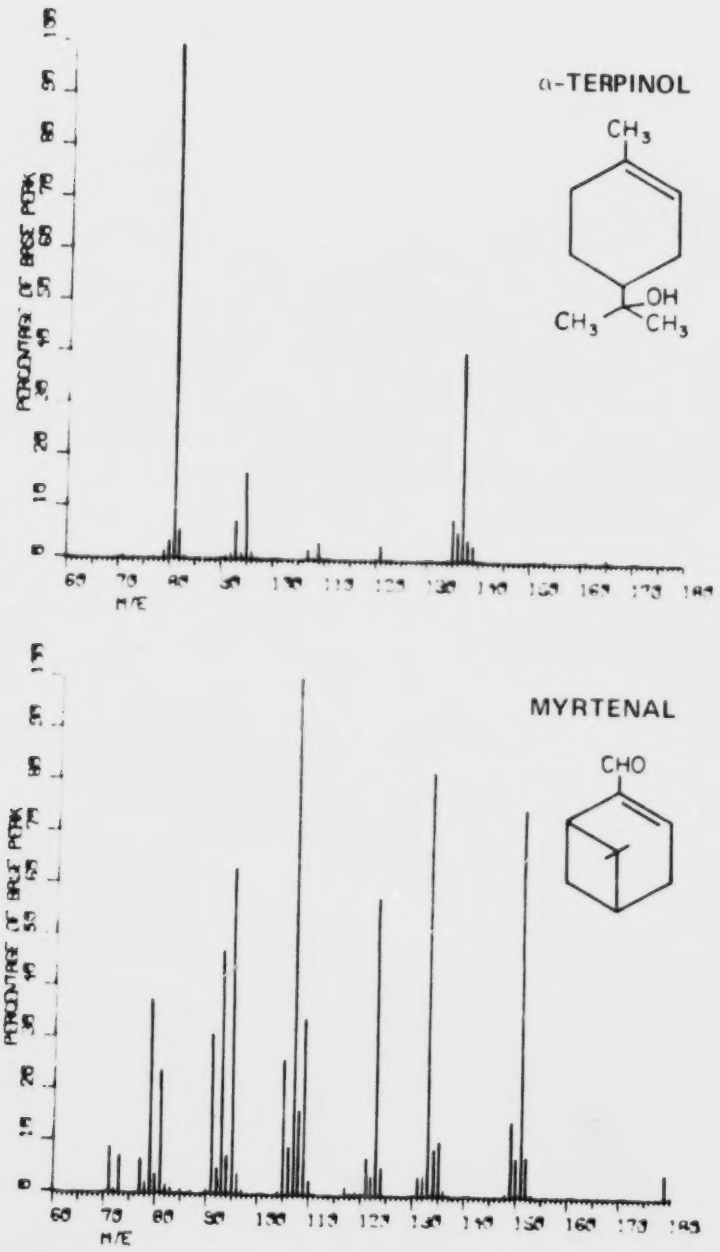


FIGURE 47. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC α-TERPINOL AND MYRTENAL.

(Refer to Chromatograms in Figure 44)

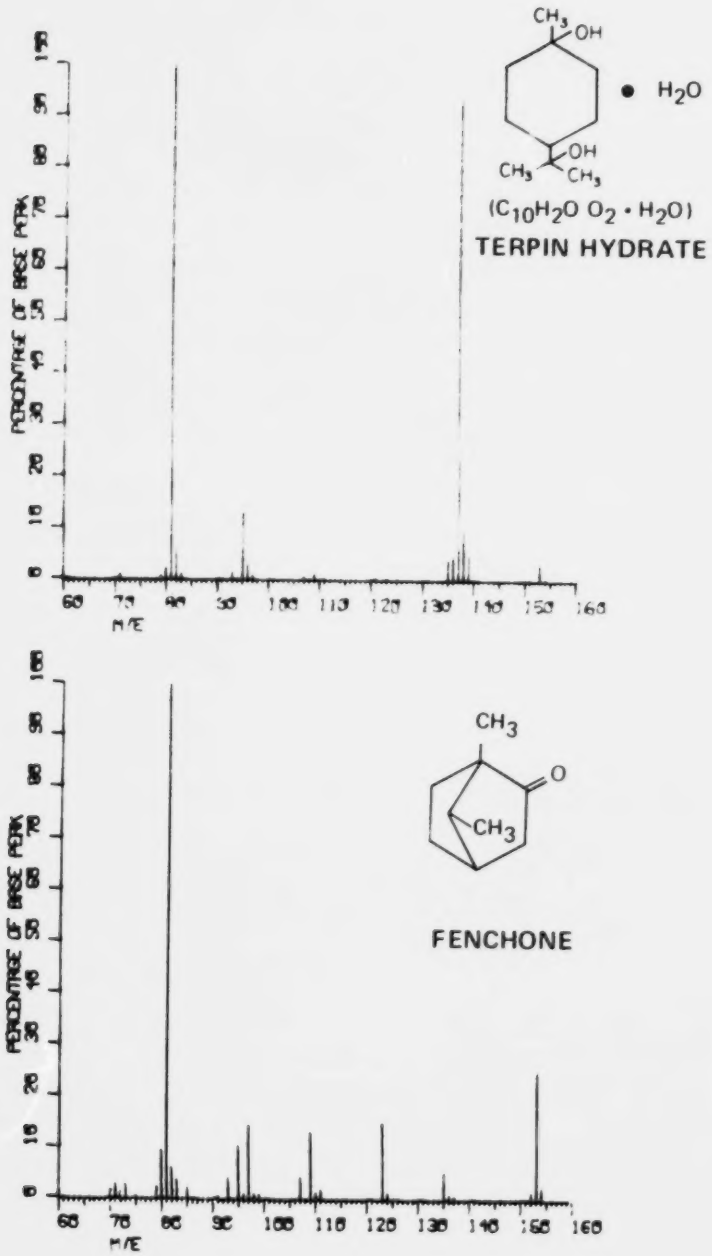


FIGURE 48. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC TERPIN HYDRATE AND FECHONE.

(Refer to Chromatograms in Figure 44)

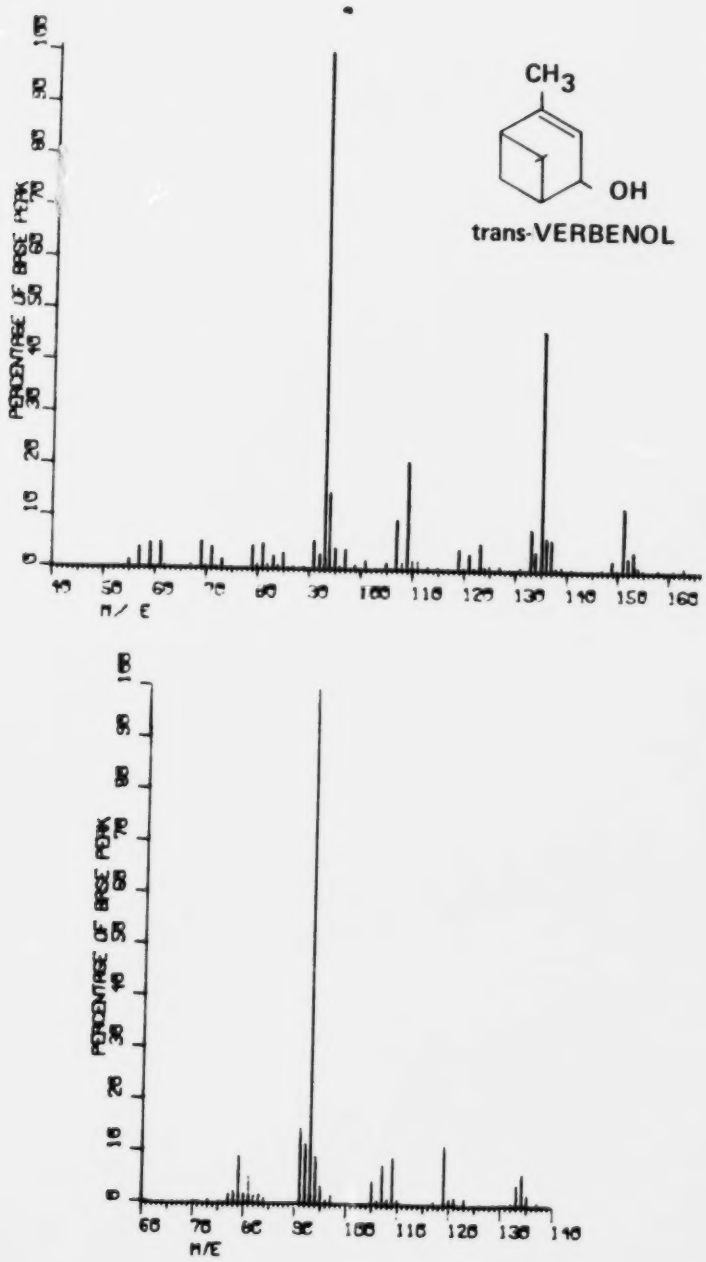


FIGURE 49. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF AUTHENTIC trans-VERBENOL.
(Refer to Chromatograms in Figure 44)

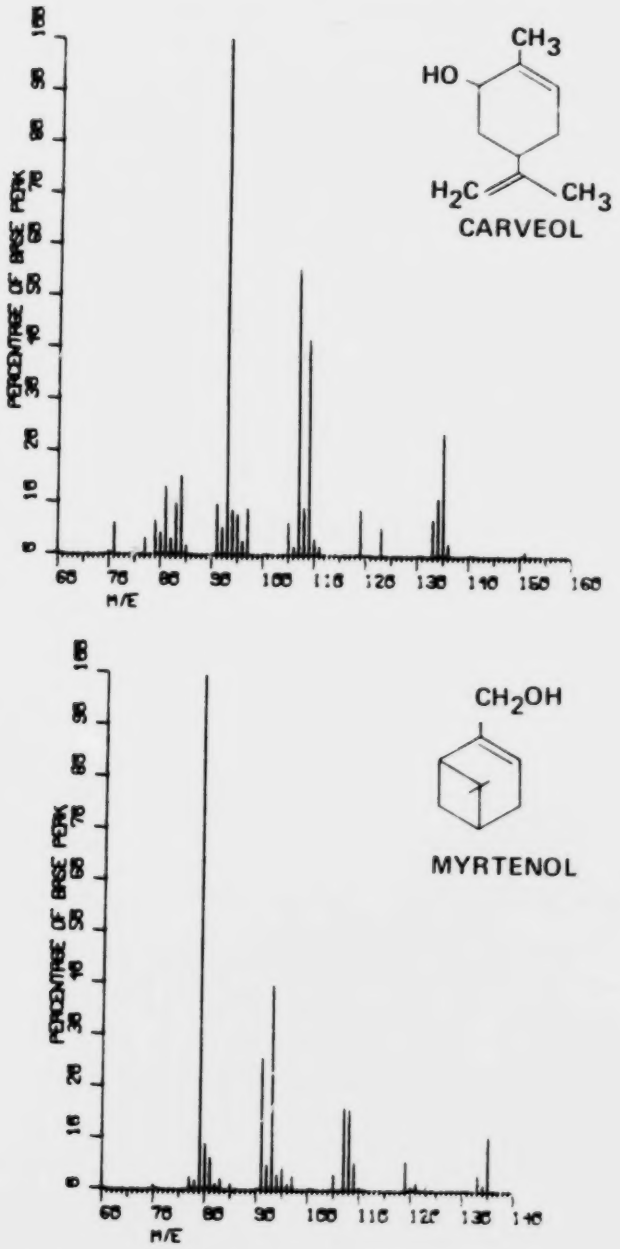


FIGURE 50. CHEMICAL IONIZATION MASS SPECTRA (METHANE) OF MYRTENOL AND CARVEOL.

(Refer to Chromatograms in Figure 44)

tentatively assigned molecular weights of the aerosol products was shown in Figure 43. Surprisingly, these comparisons did not produce any satisfactory spectral matches.

Borneol, α-fenchyl alcohol, and α-terpineol have molecular weight 154; their mass spectra are shown in Figures 46 and 47. Compare with these spectra that for chromatographic peak E shown in Figure 51 (the chromatogram is shown in Figure 43). In view of the lack of definitive fragmentation, no structure has been assigned to this aerosol product. Nevertheless, peaks at m/e 155, 183, and 195 are characteristic of a compound of molecular weight 154. A weak peak at m/e 137 is consistent with loss of H_2O and suggests the possibility that the product is an alcohol. However, the base peak of the compound is clearly at m/e 109. This fragment is rather small in each of the standard spectra. Moreover, the standard spectra show characteristic fragments at m/e 81 and 95; these fragments are absent in the product spectrum. Thus, it is highly unlikely that the product corresponds to any of the above three standards.

The mass spectrum shown in Figure 52 has been tentatively identified as pinononic aldehyde, as shown. (The spectrum will be discussed in detail, below.) There is no evidence to suggest that it corresponds to any of the above standards.

Verbenol, myrtenol, carveol, and fenchone have molecular weight 152; their spectra are shown in Figures 48-50. Compare to these spectra that for chromatographic Peak B (from Figure 43) as shown in Figure 53. Although this spectrum is weak, peaks at m/e 153 (MH^+) and 135 ($MH^+ - H_2O$) suggest the possibility of an alcohol of molecular weight 152. The product exhibits some fragmentation characteristics of all the above standard alcohols, but is most similar to verbenol. (Figure 49; note duplicate analyses of the standard.) However, in comparing the product spectrum to that of verbenol note that the peaks at m/e 101

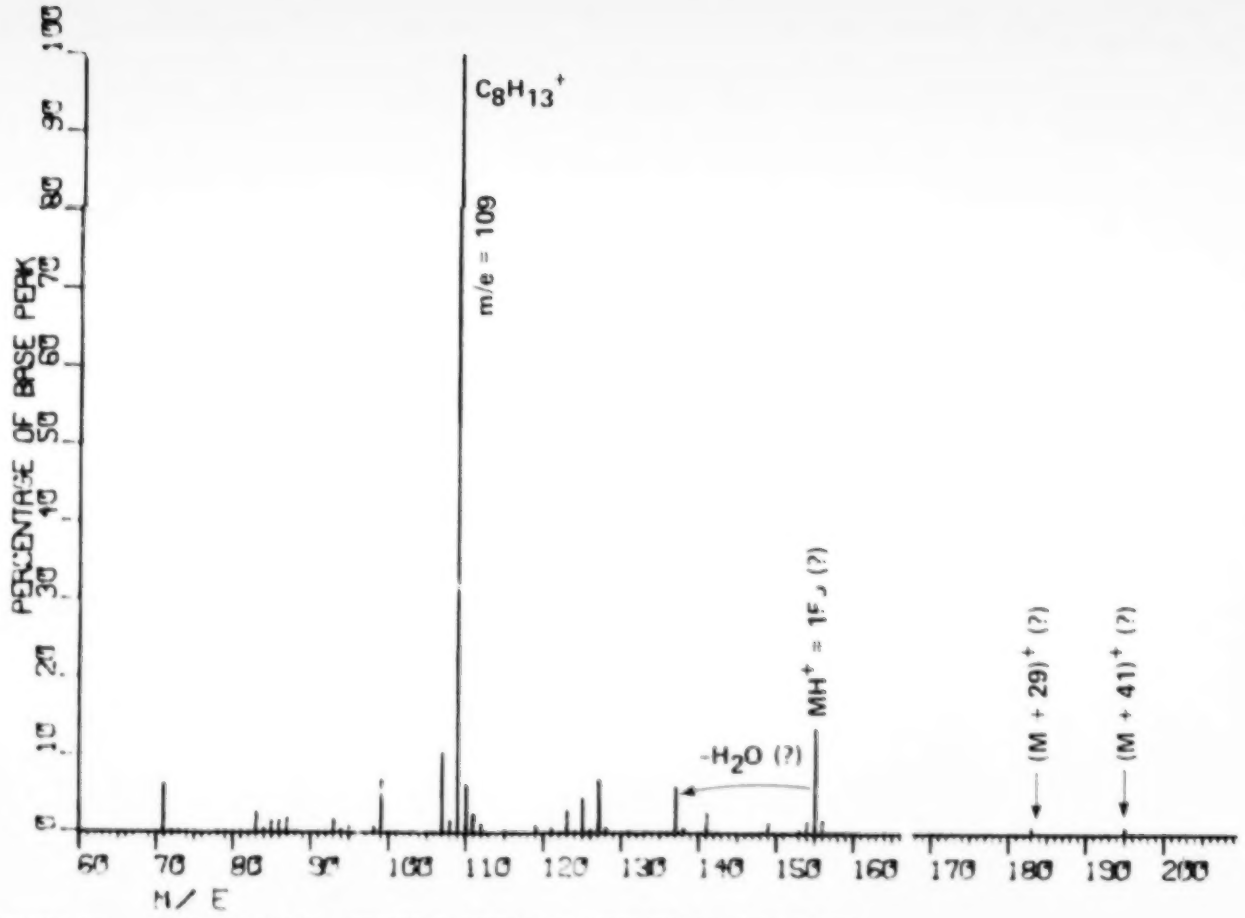


FIGURE 51. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK E.
(Refer to Chromatogram in Figure 43)

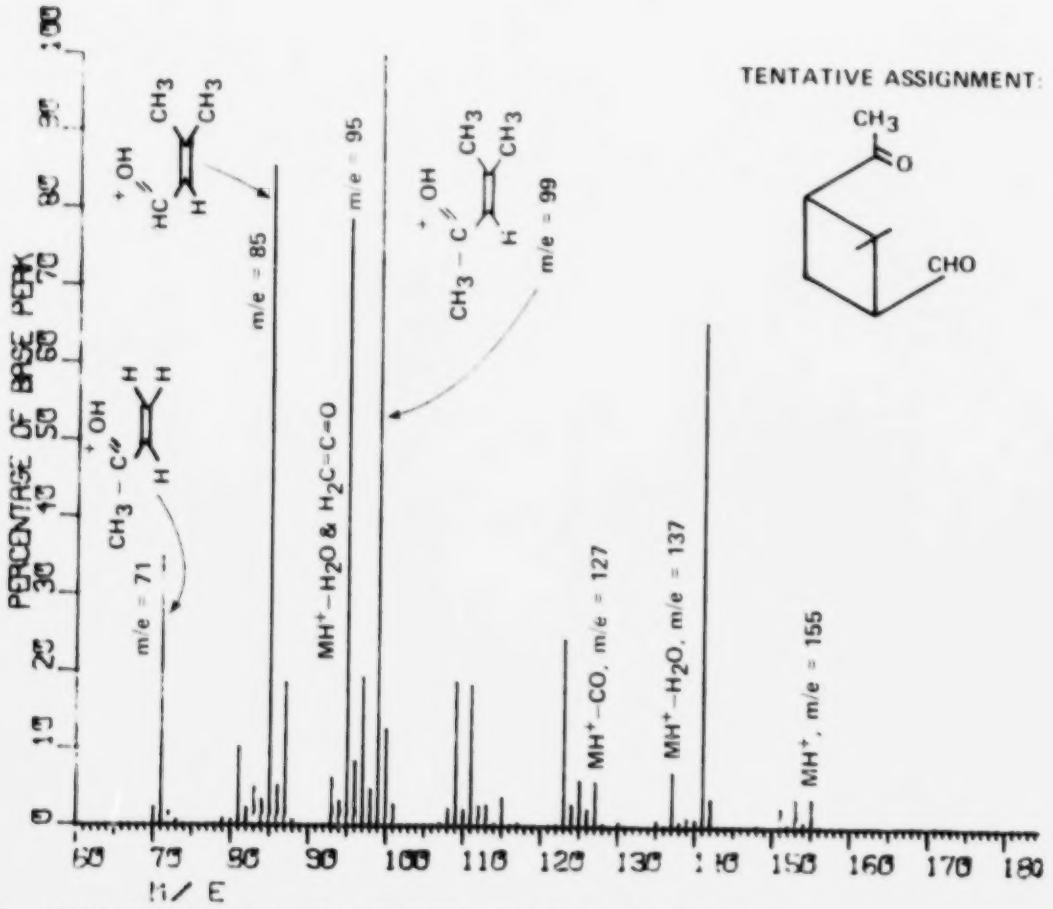


FIGURE 52. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK C.
(Refer to Chromatogram in Figure 43)

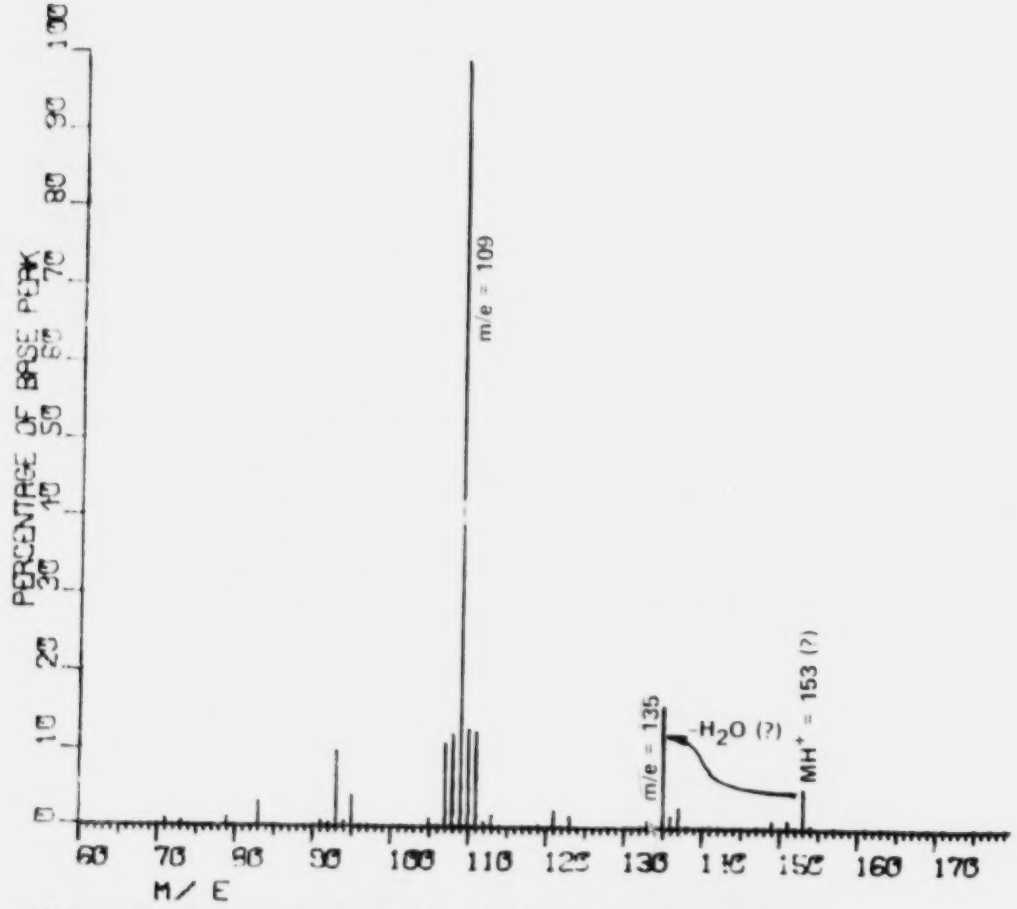


FIGURE 53. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK B.
(Refer to Chromatogram in Figure 43)

and 93 exhibit reversed intensity. Thus, assignment of the product as verbenol would be rather speculative.

The mass spectrum of chromatographic Peak A (from Figure 43) is shown in Figure 54. The spectrum is rather ambiguous and does not permit assignment of a structure; the molecular weight may be 152. Observed fragmentation is entirely inconsistent with the above reference compounds.

Myrtenal was a molecular weight of 150. Limonene and terpinoline have molecular weight 136. Their mass spectra are shown in Figures 45 and 47. The mass spectra for the α-pinene neutral fraction did not indicate the presence of any components with these molecular weights.

In concluding this discussion, it should be emphasized that mass spectral fragmentation patterns observed for various terpenoids have tended to be somewhat variable from one analysis to the next. Fragmentation of these compounds is especially sensitive to instrument variability. This can be seen in spectra for trans-verbenol obtained upon duplicate analyses (Figure 49). In the illustrated case, the analyses were made about 1 year apart during different research programs. During the current work, analyses of standards and unknowns were performed over a period of several days, and reanalysis of standards was conducted. Nevertheless, in analysis of these sensitive compounds, there is a possibility that slight instrument variabilities may be significant. Thus, it is not possible to completely rule out the presence of the reference compounds in the reaction mixture. Reanalysis of materials in hand with special attention to instrument conditions should help to eliminate the present ambiguity concerning this phase of the study.

Tentative Assignments for α-Pinene Neutral Products--Although the above studies of authentic compounds have not led to unambiguous

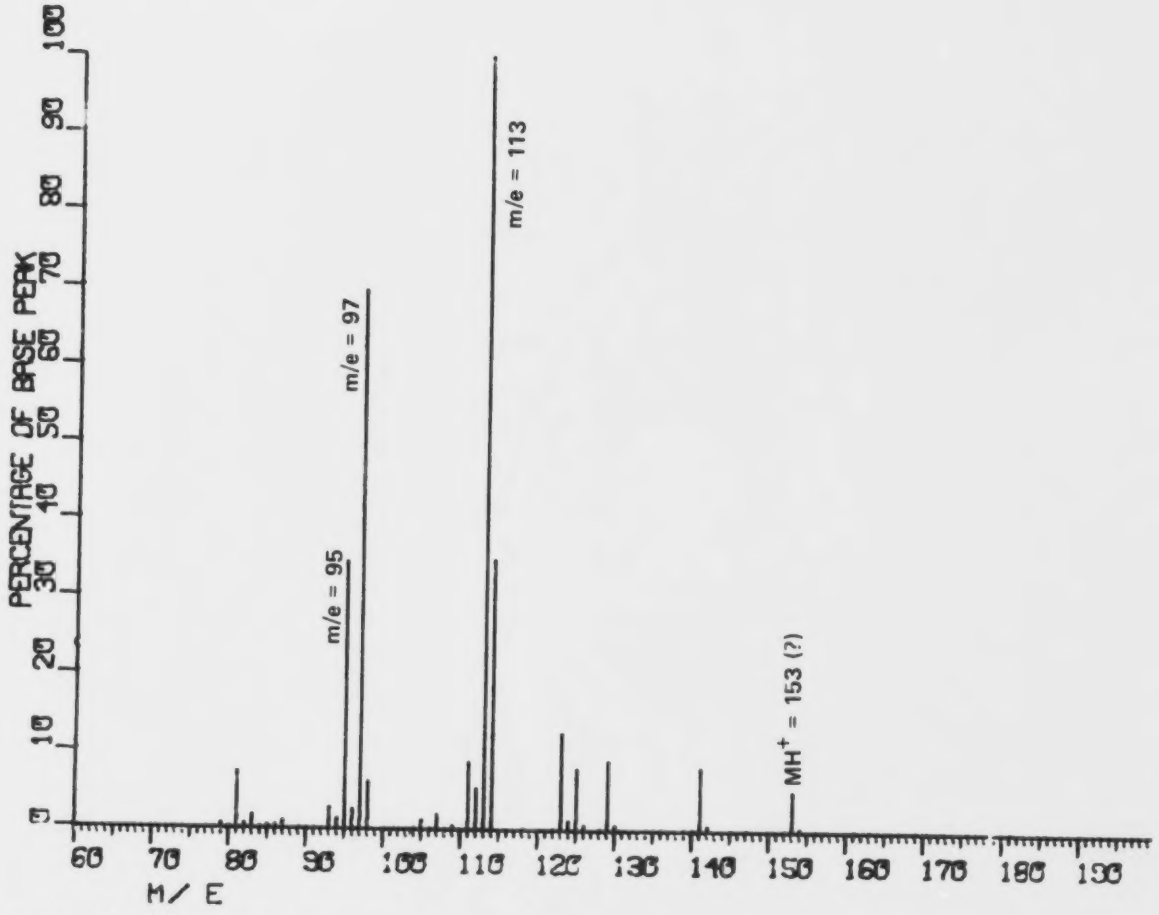


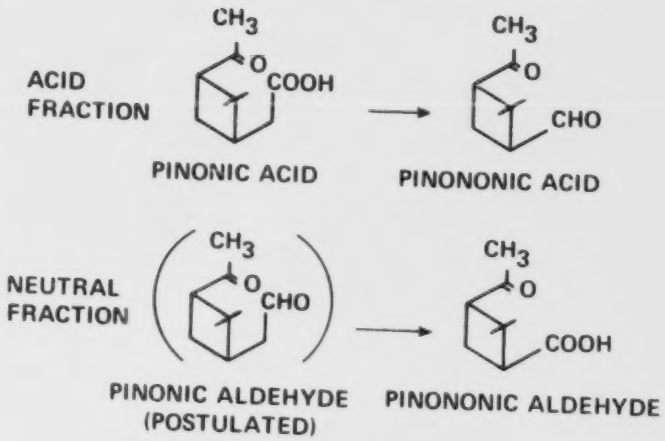
FIGURE 54. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK A.
(Refer to Chromatogram in Figure 43)

identification of α-pinene reaction products, tentative assignments for various products are considered in this section. Some are based upon comparison of the sample fragmentation pattern with that observed for authentic methyl pinonate. An especially helpful diagnostic has been the fragmentation arising from (proposed) transannular cleavages. In examining the mass spectra shown in Figures 52 and 55-58 below, it may be helpful to refer to Table 4 (p.85) in which the fragmentation of authentic methyl pinonate is rationalized.

As a point of departure, it would be reasonable to expect formation of pinonic aldehyde, as shown below. Formation of this compound would be analogous to formation of pinonic acid as observed in the acid fraction.

Pinonic aldehyde has a molecular weight of 168. As indicated in Figure 43, six components of the neutral fraction have been tentatively assigned molecular weights of this value. Fragmentation patterns of these components have not permitted unambiguous assignment of the proposed structure to any of the six candidate products. Nevertheless, there is a strong likelihood that this compound is indeed involved in the aerosol reactions of α-pinene.

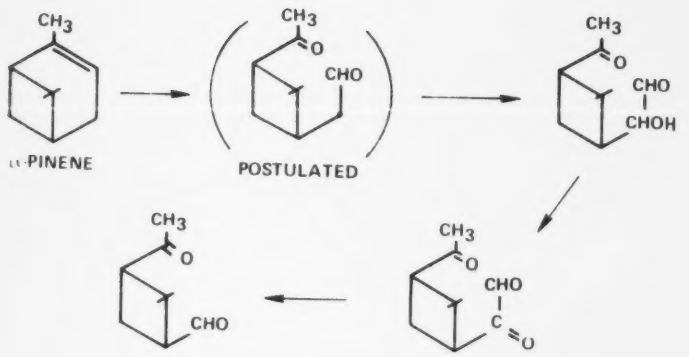
Consider the mass spectrum in Figure 52. This corresponds to Peak C in the reconstructed gas chromatogram Figure 43. The compound is tentatively identified as pinononic aldehyde. Fragmentation appears to be analogous to that of authentic methyl pinonate. Key fragments are rationalized in the figure. This product might arise from oxidative degradation of the homologous dicarbonyl, as indicated below. Its formation might be considered analogous to formation of pinononic acid, observed in the acid fraction.



Consider next, the mass spectrum shown in Figure 55. This corresponds to Peak F in the reconstructed gas chromatogram. The tentatively assigned structure is shown. As in the previous case, the fragmentation is rationalized in the figure, and appears to be analogous to that of methyl pinonate.

Finally, consider the mass spectrum shown in Figure 56. This corresponds to Peak G in the reconstructed gas chromatogram (Figure 43). Again, the tentative assignment is based on comparison of the indicated fragments to those of authentic methyl pinonate.

In view of the last three proposed assignments, it is not unreasonable to present the scheme shown below. This scheme is not meant to suggest mechanistic considerations, but is clearly a possible route for the formation of a series of sequentially degraded oxidation products.



Formation of the proposed products shown above involve, in each case, cleavage of the carbon-carbon double bond. Studies cited earlier indicated that α-pinene can undergo "autooxidation" in the presence of air, moisture, and sunlight to yield sobrerol (see p. 93). Formation of this product involves cleavage of the cyclobutane ring with retention of an intact carbon-carbon double bond. If the cyclobutane ring were cleaved at the alternative internal position, an isomeric diol might additionally be formed, as shown in the structures below. Further oxidation or oxidation/dehydration might be expected to yield the compounds shown below.

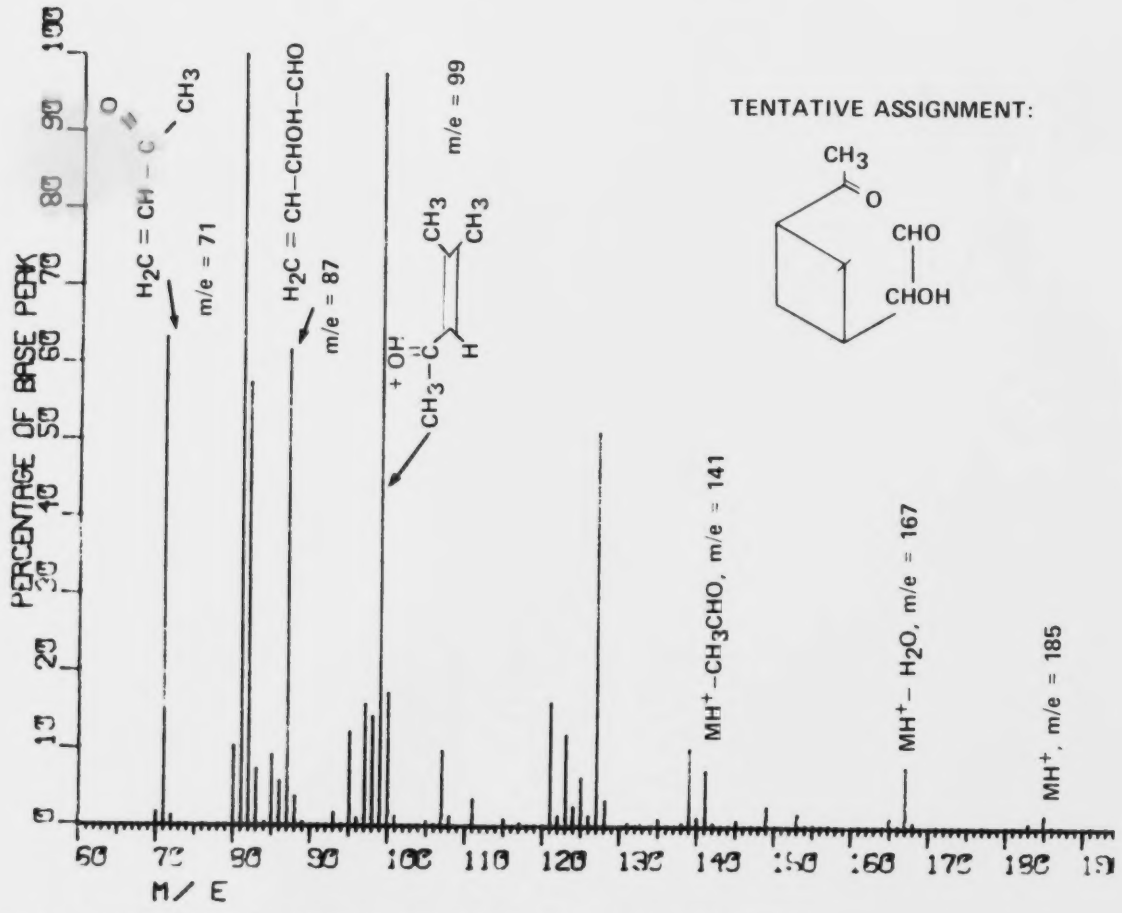


FIGURE 55. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK F.
(Refer to Chromatogram in Figure 43)

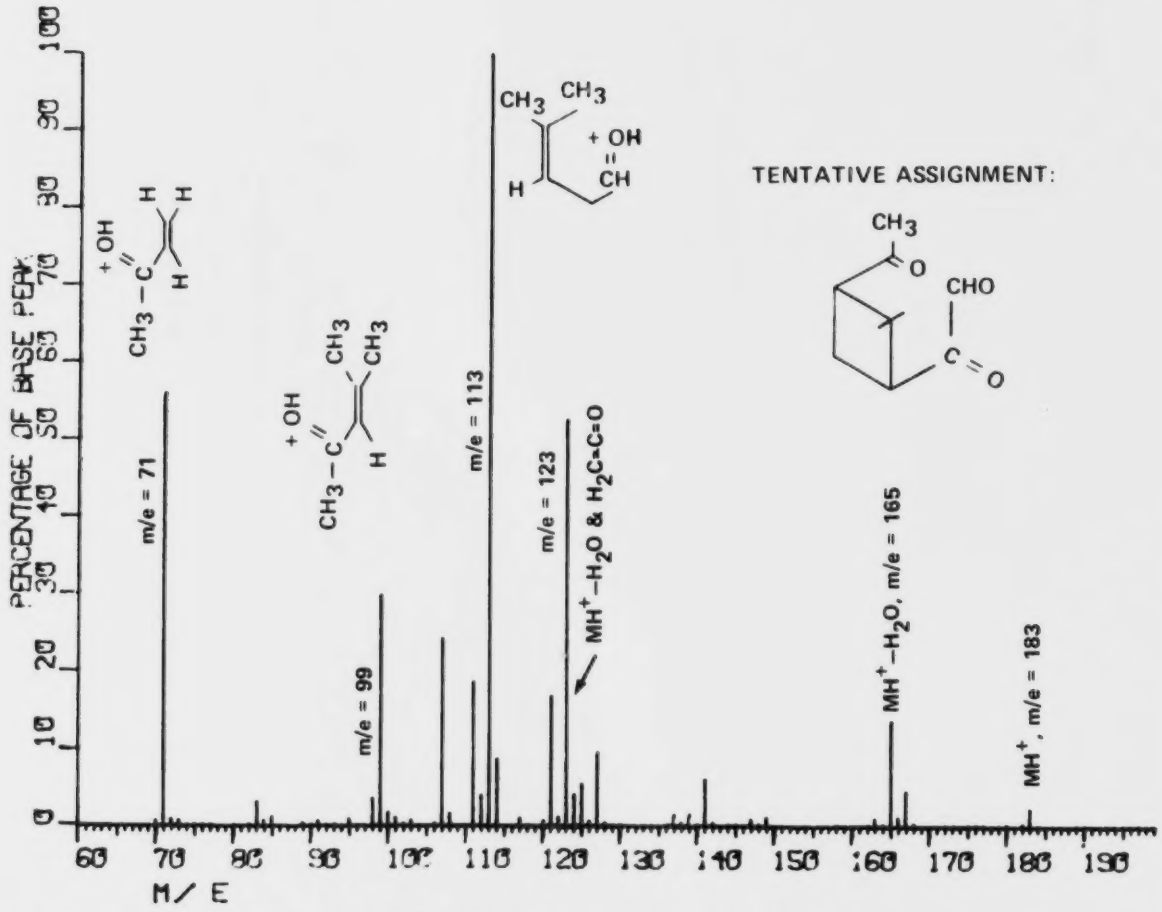
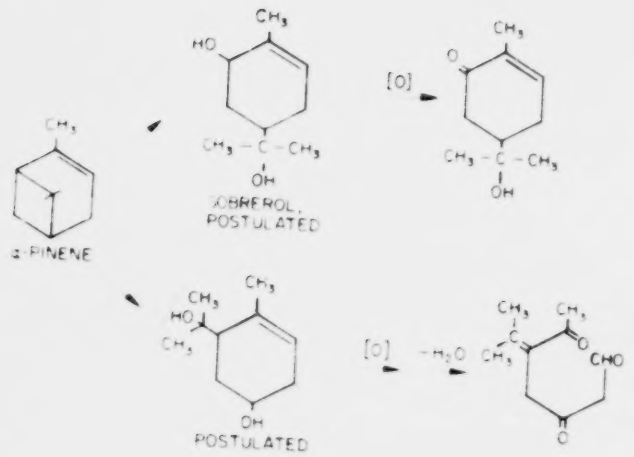


FIGURE 56. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK G.
(Refer to Chromatogram in Figure 43)



Mass spectra tentatively identified as consistent with these structures are shown in Figures 57 (hydroxycarvotanacetone) and 58, Peaks D and H in Figure 43. Rationalization of fragmentation is presented in the figures. Spectral interpretation in these cases, would be greatly aided by availability of a spectrum of authentic sobrerol for comparison. As mentioned previously, no commercial sample of this compound could be obtained. It is noteworthy, however, that in these last two spectra, the diagnostic fragments associated with the presence of an intact cyclobutane ring (i.e., transannular cleavage fragments at m/e$^-$ 71 and 99; see Tables 4 and 5) are absent or very weak.

Thus, we suggest that under simulated atmospheric conditions, α-pinene reactions include cleavage of the cyclobutane ring, and that such cleavage may occur with retention of the carbon-carbon double bond.

α-Pinene Basic Fraction

Of the model aerosol systems studied, only in the case of α-pinene was there sufficient material obtained to permit analysis of the basic fraction (see Table 3 p.29). Although the basic fraction was negligibly small in all cases, analysis of the basic fraction for at least

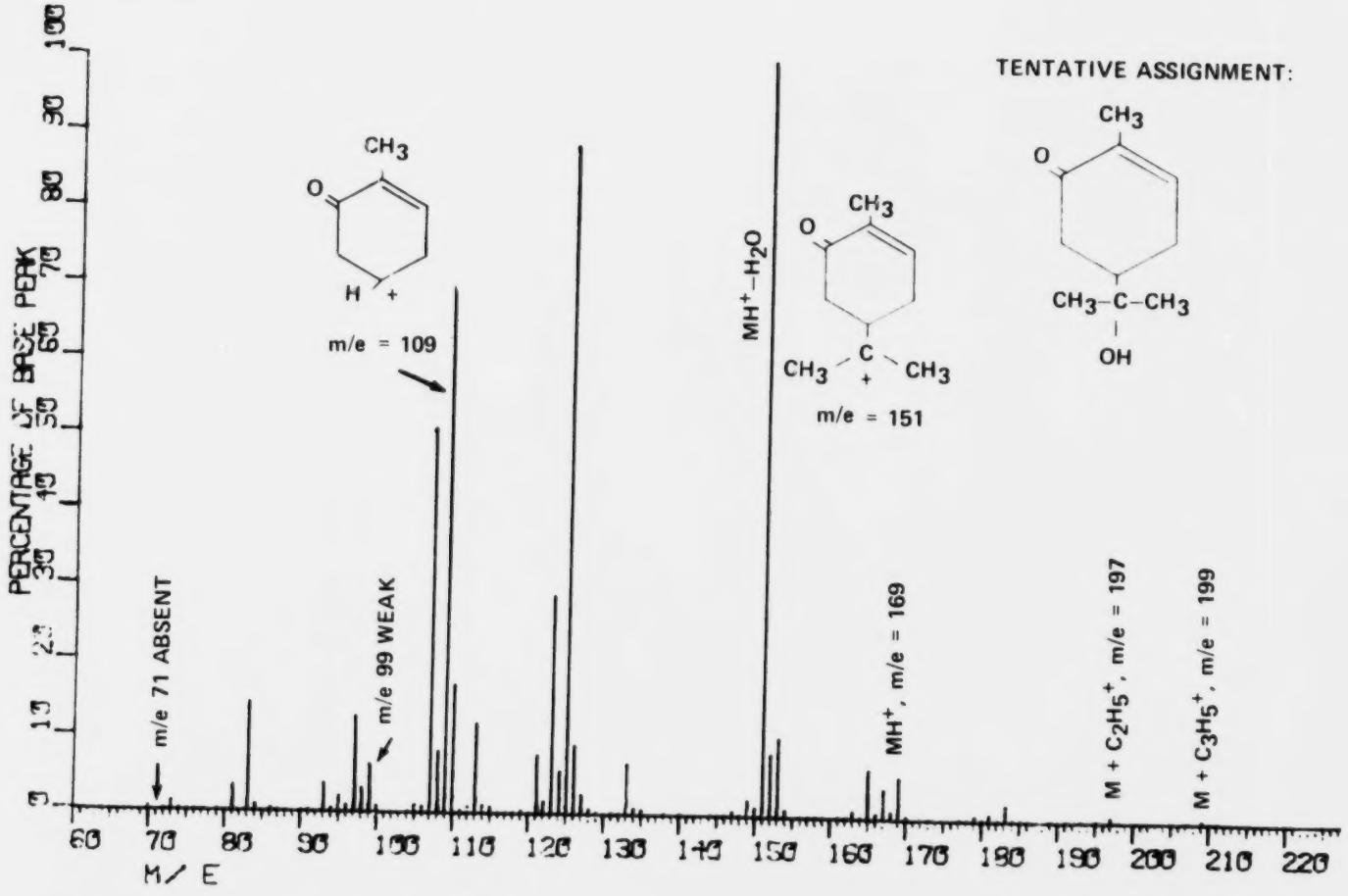


FIGURE 57. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK D.
(Refer to Chromatogram in Figure 43)

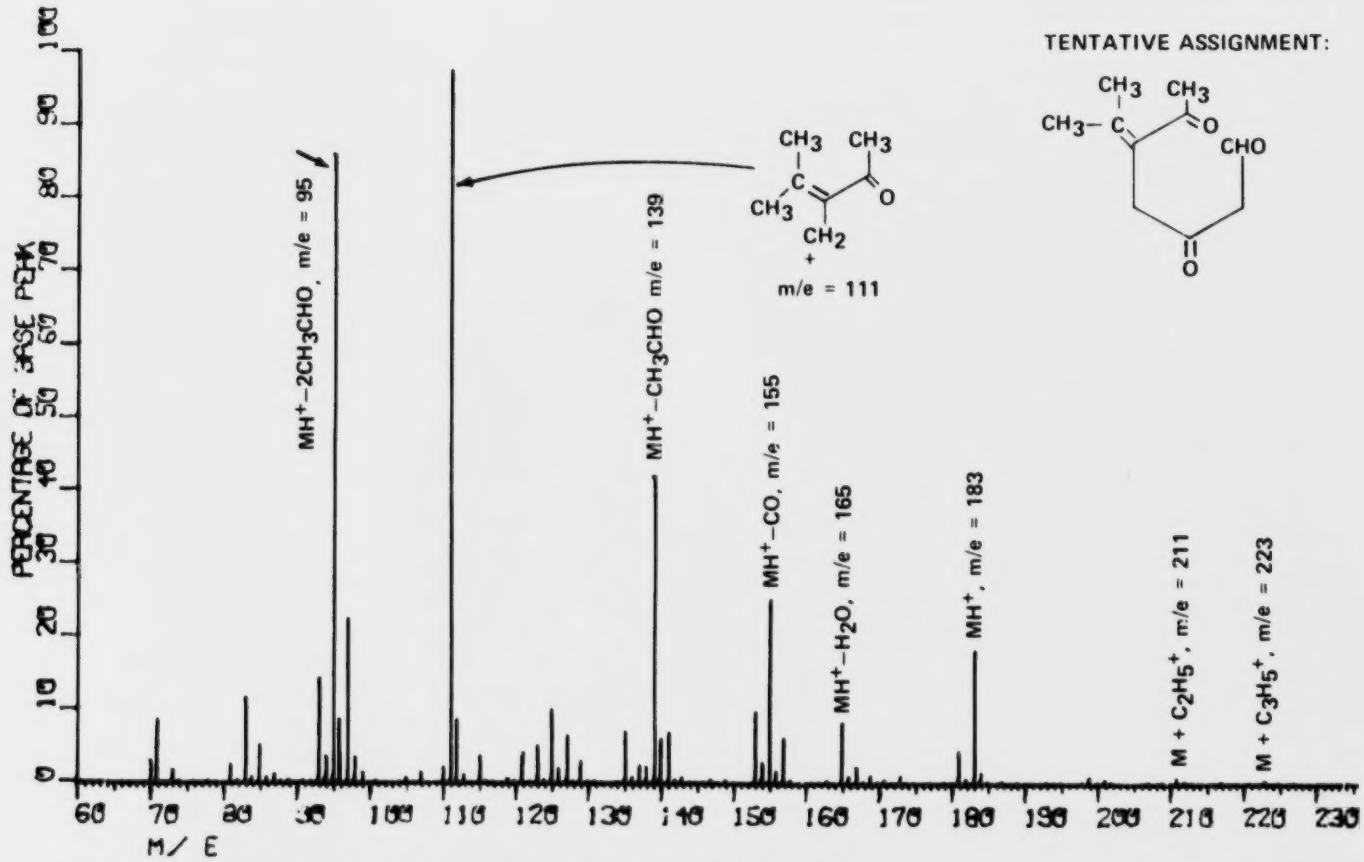


FIGURE 58. ANALYSIS OF α-PINENE AEROSOL, NEUTRAL FRACTION. CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK H.

(Refer to Chromatogram in Figure 43)

one aerosol was desirable to determine if any nitrogen bases were indeed formed under atmospheric simulation.

Analysis of the α-pinene basic fraction by GC-MS did not suggest the presence of any nitrogen bases, nor indeed, the presence of any nitrogen containing products. The spectra obtained are in fact typical of those observed for the α-pinene neutral fraction. That is, the "basic" fraction appears to be composed primarily of neutral reaction products. This can be explained by reference to the fractionation procedure.

As described previously, a methylene chloride solution of the water-insoluble aerosol products was extracted with dilute aqueous sodium hydroxide and with dilute hydrochloric acid. The basic fraction was defined as that material extracted into the dilute acid. During the acid extraction, a small quantity of (insoluble) neutral material was apparently entrained or emulsified in the dilute acid wash, and was thereby carried along with the "basic" fraction. In future work, this will be avoided by carefully backwashing the dilute acid phase with solvent before the aqueous phase is made alkaline and extracted with solvent. An analogous backwashing procedure will be used in the isolation of the acid fraction. In summary, it appears that if any genuinely basic products are formed, their concentration is vanishingly small in the material analyzed.

Several representative mass spectra obtained for this fraction are presented in order to illustrate the "neutral" character of the components. The reconstructed gas chromatogram is shown in Figure 59. Consider the mass spectrum shown in Figure 60, corresponding to chromatographic Peak A. The spectrum is extremely similar to that observed for the neutral product considered earlier in Figure 52. A fragment consistent with the protonated parent ion is observed at m/e 155 and peaks consistent with loss of carbon moroxide and water are observed at m/e 127 and 137 respectively. Key fragments consistent with

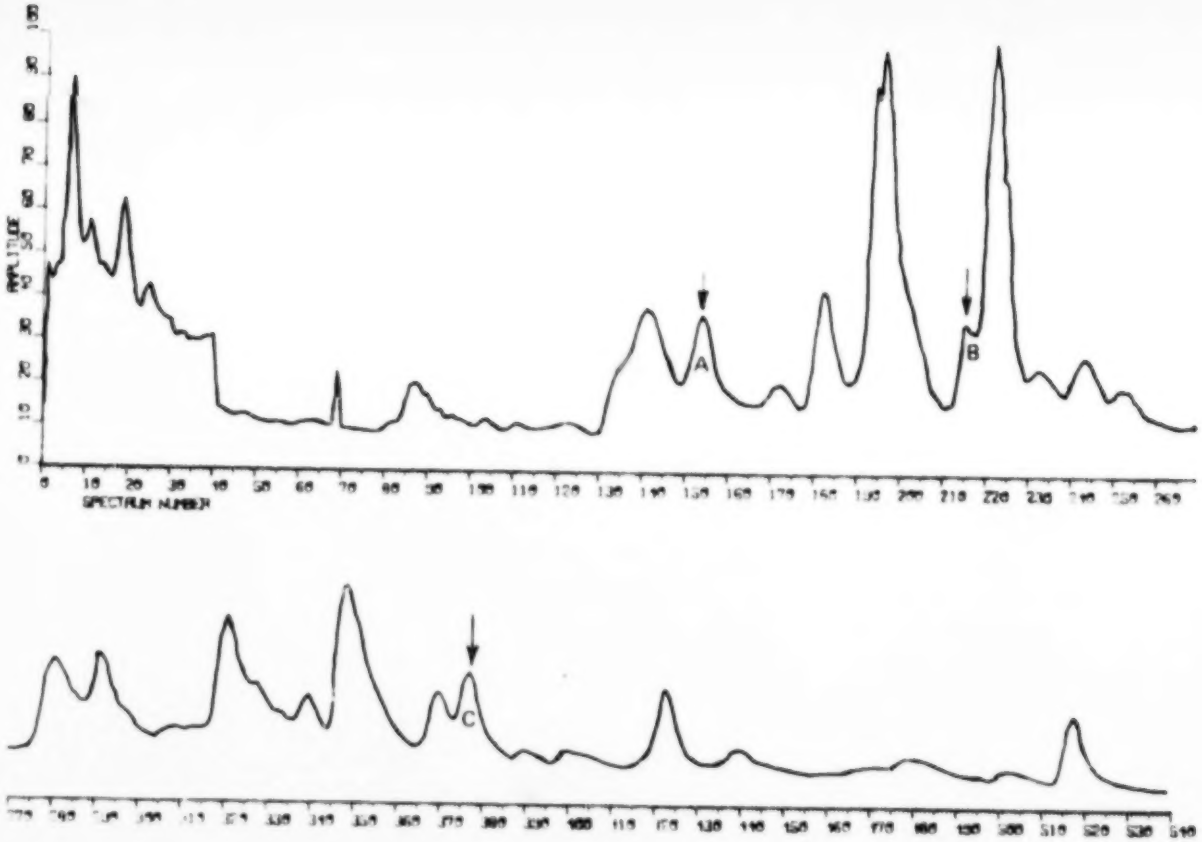


FIGURE 59. ANALYSIS OF α-PINENE AEROSOL, BASIC FRACTION. RECONSTRUCTED GAS CHROMATOGRAM FOR METHANE CI-MS.

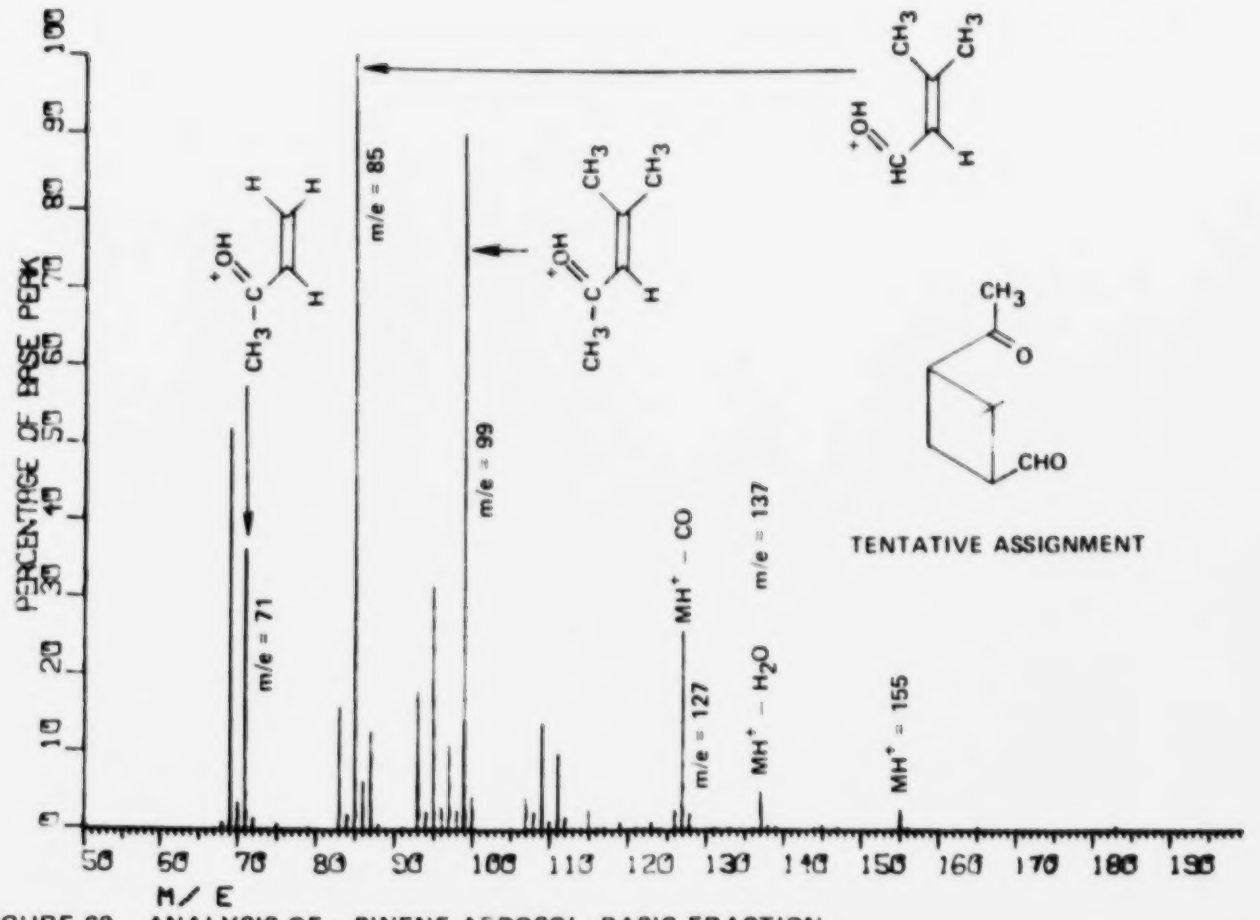


FIGURE 60. ANALYSIS OF α-PINENE AEROSOL, BASIC FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK A.
(Refer to Chromatogram in Figure 59)

transannular cleavage are observed at m/e 71, 85, and 99. Thus, the product is tentatively assigned the structure shown, identical to that proposed in Figure 52.

Consider the mass spectra shown in Figure 61; they correspond to chromatographic Peak B. The upper spectrum was obtained using methane as the chemical-ionization reagent gas. The lower spectrum was obtained using helium as the reagent gas; hence it is much like an electron-impact spectrum. The methane spectrum is consistent with a molecular weight of 138, although the satelite peak at (M + 29) is very weak. Using the Battelle peak-matching program, the helium spectrum was compared with a computerized file of 11,000 electron-impact spectra. The sample spectrum corresponded very closely with that of terpinoline. Consistent with this finding and with the apparent molecular weight determined from the methane spectrum, the product is tentatively assigned as terpinoline.

Finally, consider the spectrum shown in Figure 62 corresponding to chromatographic Peak C. The structure shown in the figure is especially tentative. The peak assigned as the protonated parent ion is consistent with a molecular weight of 182. Fragments consistent with loss of H_2O and loss of $CH_2=C=O$ plus H_2O are observed. Peaks diagnostic of an intact cyclobutane ring are absent. Consistent with these data, a speculative structure is shown.

The above described spectra are typical of those observed for the "basic" fraction. The results suggest that this fraction consists principally of a small quantity of neutral product carried over during an incomplete fractionation step.

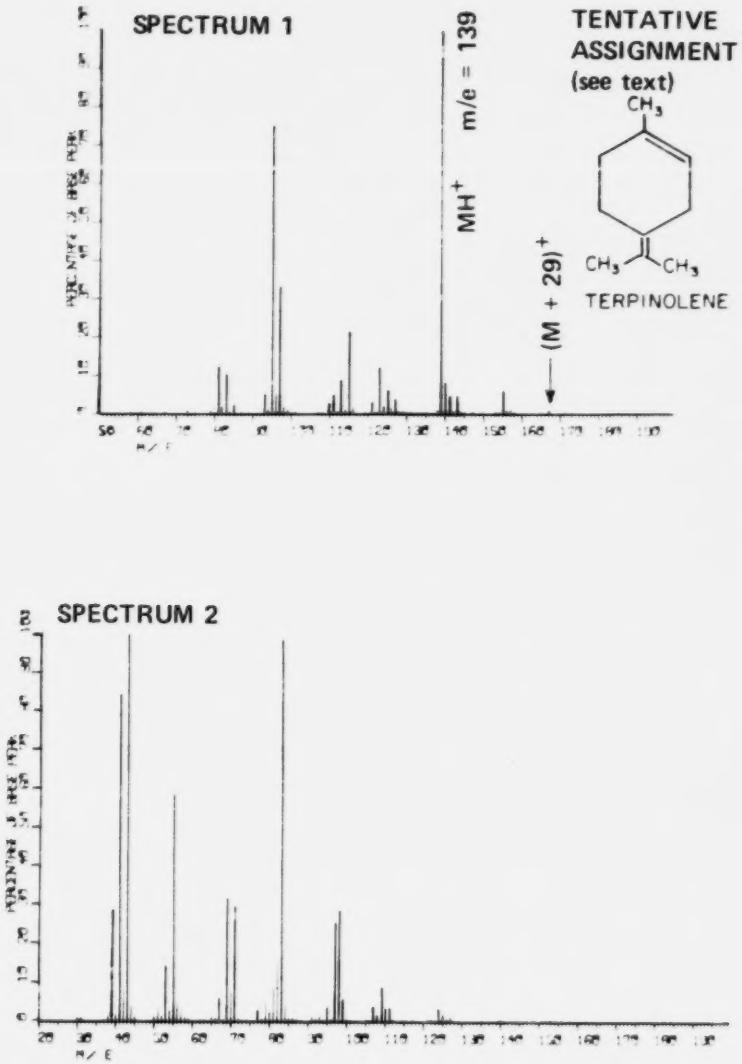


FIGURE 61. ANALYSIS OF α-PINENE AEROSOL, BASIC FRACTION.
CHEMICAL IONIZATION MASS SPECTRA FOR CHROMATOGRAPHIC PEAK B.
SPECTRUM 1 BY METHANE CI-MS, SPECTRUM 2 BY HELIUM CI-MS.
(Refer to Chromatogram in Figure 59)

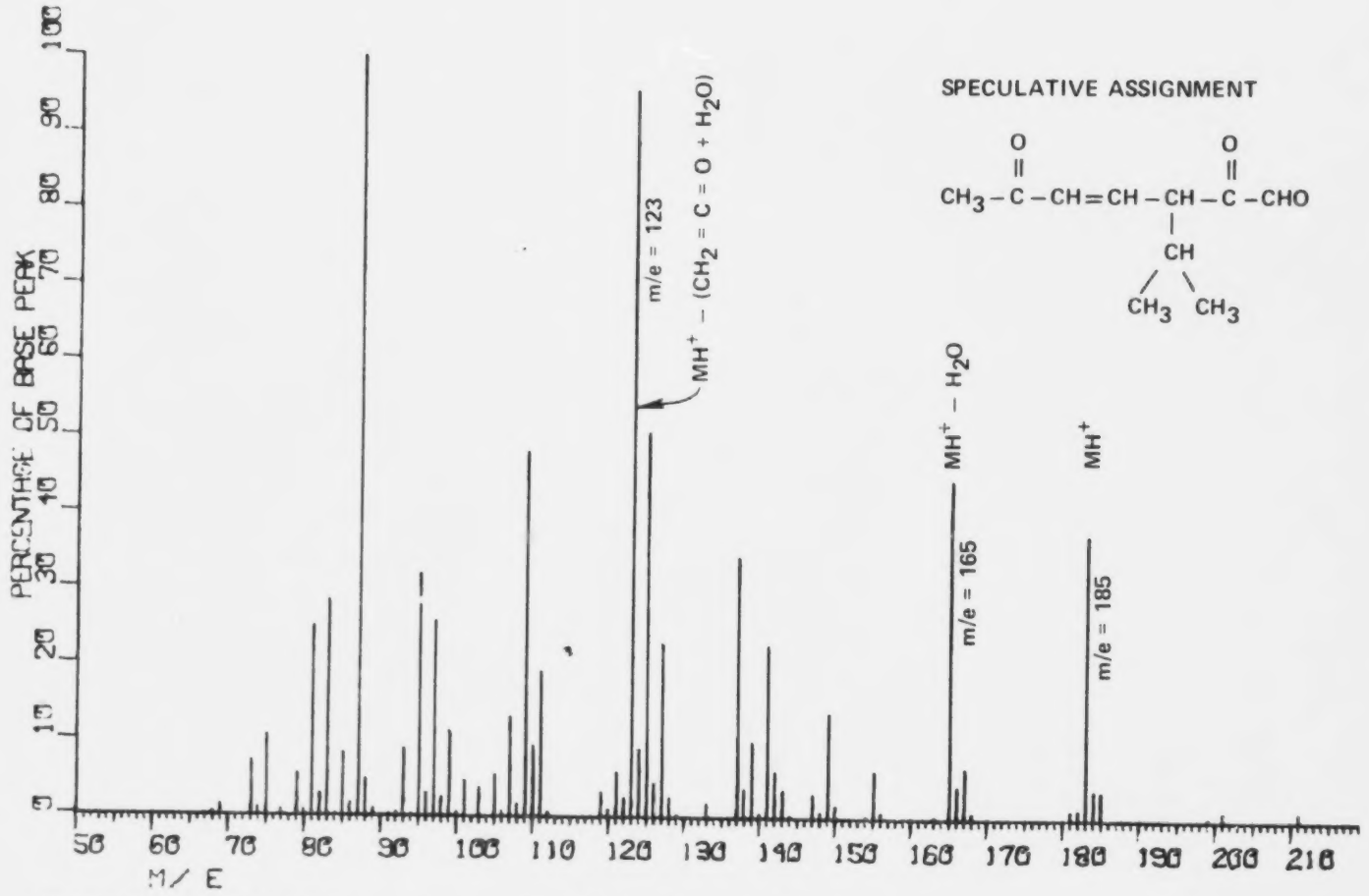


FIGURE 62. ANALYSIS OF α-PINENE AEROSOL, BASIC FRACTION.
CHEMICAL IONIZATION MASS SPECTRUM (METHANE) FOR CHROMATOGRAPHIC PEAK C.
(Refer to Chromatogram in Figure 59)

SECTION V

REFERENCES

(1) Schuetzle, D., Crittenden, A. L., Cronn, D. R., and Charlson, R. J., "Molecular Composition of Secondary Aerosol and Its Origin", paper presented at the 172nd National A.C.S. Meeting; Chicago, Illinois; August 1973.

(2) Air Pollution Control District, Los Angeles County, "Effectiveness of Organic Solvents in Photochemical Smog Formation", Solvent Project, Final Report, 1966.

(3) Altshuller, A. P., Bufalini, J. J., Environ. Sci. Technol., 5, 39 (1971).

(4) Altshuller, A. P., Bufalini, J. J., Photochem. Photobiol., 4, 97 (1965).

(5) Altshuller, A. P., Cohen, R. R., presented at American Chemical Society Meeting, Division of Water, Air, and Waste Chemistry, New York, New York, Sept. 8-13, 1963.

(6) Altshuller, A. P., Klosterman, D. L., Leach, P. W., Hindawi, I. J., Sigsby, J. E., Jr., Int. J. Air Water Pollut., 10, 81 (1966).

(7) Altshuller, A. P., Kopczynski, S. L., Lonneman, W. A., Becker, T. L., Wilson, D. L., Environ. Sci. Technol., 2, 696 (1968).

(8) Doyle, G. J. and Renzette, N. A., Air Pollut. Contr. Assoc., 8, 23 (1968).

(9) Endow, N., Doyle, G. S., Jones J. L., ibid, 13, 141 (1963).

(10) Goetz, A., Pueschel, R. F., Atmos. Environ., 1, 287 (1967).

(11) Groblicki, P. J., Nebel, G. J., presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, GMC, Warren, Mich., Oct, 6 and 7, 1969.

(12) Harkins, J., Nicksic, S. W., J. Air Pollut. Contr. Assoc., 15, 218 (1965a).

(13) Harkins, J., Nicksic, S. W., presented at American Chemical Society Meeting, Division of Petroleum Chemistry, Detroit, Michigan, April 4-9, 1965b.

(14) Hayakawa, I., J. Air Pollut. Contr. Assoc., 14, 339 (1964).

(15) Johnston, H. S., der Jain, K., Science, 131, 1523 (1960).

(16) Orr, C., Jr., Hurd, F. K., Corbett, W. J., J. Colloid Sci., 13. 472 (1968).

(17) Prager, M. J., Stephens, E. R., Scott, W. E., Ind. Eng. Chem.. 52, 521 (1960).

(18) Renzetti, N. A., Doyle, G. J., Int. J. Air Pollut. 2, 327 (1960).

(19) Ripperton, L. A., Decker, C. E., Page, W. W., presented at American Chemical Society Meeting, Division of Water, Air, and Waste Chemistry, Atlantic City, N. J., Sept. 13-17, 1962.

(20) Schuck, E. A., Ford, H. W., and Stephens, E. R., "Air Pollution Effects of Irradiated Automobile Exhaust as Related to Fuel Composition", Air Pollution Foundation Report 26, October, 1958.

(21) Stephens, Edgar R., Price, Monty A., Atmos. Environ. 3, 573 (1969). Stern, A. C., ed., "Air Pollution", Vols I-III, 2nd Ed., Academic Press, New York, New York, 1968.

(22) Stevenson, H.J.R., Sanderson, D. E., Altshuller, A. P., Int. J. Air Water Pollut., 9, 367 (1965).

(23) Timmons, R. G., presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, GMC, Warren, Mich., Oct. 6 and 7, 1969.

(24) Wayne, L. G., and Romanovsky, J. C., "Rates of Reaction of the Oxides of Nitrogen in Photo-oxidation of Diluted Automobile Exhaust Gases", Chemical Reactions in the Lower and Upper Atmosphere, Interscience, New York, 1961, p. 71.

(25) Wilson, Wm. E., Jr., Merryman, E. L., Levy, A., J. Air Pollut. Cont. Assoc., 21, 3 (1971).

(26) Wilson, Wm. E., Jr., Miller, D. F., Trayser, D. F., and Levy, A., "A Study of Motor Fuel Composition Effects on Aerosol Formation. Part III Visibility Reduction from Automobile Exhaust". Battelle, Columbus Laboratories Report to the American Petroleum Institute Committee for Air and Water Conservation (February 1972).

(27) Wilson, Wm. E., Jr., Levy, A., "A Study of Sulfur Dioxide in Photochemical Smog", American Petroleum Institute, Project S-11, Battelle, Columbus Laboratories, Columbus, Ohio, 1968.

(28) Miller, D. F., Levy, A., and Wilson, Wm. E., Jr., "A Study of Motor Fuel Composition Effects on Aerosol Formation. Part II, Aerosol Reactivity Study of Hydrocarbons", Battelle, Columbus Laboratories Report to the American Petroleum Institute Committee for Air and Water Conservation (February 21, 1972).

(29) Levy, A. and Miller, S. E., "Final Technical Report on the Role of Solvents in Photochemical Smog Formation", to National Paint, Varnish, and Lacquer Association, Battelle, Columbus Laboratories, Columbus, Ohio, 1970.

(30) Landstrom, D. K. and Kohler, D., "Electron Microprobe Analysis of Atmospheric Aerosols", to National Air Pollution Control Administration (CPA-22-69-33) (1969).

(31) Henry, W. M. and Blosser, E. R., "A Study of the Nature of the Chemical Characteristics of Particulate Collected from Ambient Air", to National Air Pollution Control Administration (CPA-22-69-153) (1970).

(32) Schuetzle D., Cuttenden, A. L., and Charlson, R. J., "Application of Computer Controlled High-Resolution Map Spectrometry to the Analysis of Air Pollutants", J. Air Poll. Control Assoc., 23 (1970).

(33) Schwartz, W. E., Jones, P. W., Riggle, C. J., and Miller, D. F., "The Organic Composition of Model Aerosols", invited paper presented at the Eastern Analytical Symposium, New York, New York, November 1973.

(34) Wilson, Wm. E., Jr., Schwartz, W. E., and Kinzer, G. W., "Haze Formation -- Its Nature and Origin", a Battelle-Columbus Report to the Environmental Protection Agency (CPA 70-Neg. 172) and The Coordinating Research Council (CAPA 6-68) January 1972. Reference is made to results of research conducted during the contract period June 1972 - June 1973 and presented in the first annual report.

(35) Wilson, W. E., Jr., Miller, D. F., Levy, A., and Stone, R. K., "The Effect of Fuel Composition on Atmospheric Aerosol Due to Auto Exhaust", J. Air Poll. Control Assoc., 23, 949 (November 1973).

(36) Lonneman, W. A., Kopczynski, S. L., Darley, P. E., and Sutterfield, F. D., "Hydrocarbon Composition of Urban Air Pollution", Environ. Sci and Technol., 8, 229 (March 1974).

(37) Kopczynski, S. L., Lonneman, W. A., Sutterfield, F. D., and Darley, P. E., "Photochemistry of Atmospheric Samples in Los Angeles", Environ. Sci. and Technol., 6, 342 (April 1972).

(38) Rasmussen, R. A., J. Air Poll. Control Assoc., 22, 537 (1972).

(39) Rasmussen, R. A., Proc. Nat. Acad. Sci.,53, 215 (1965).

(40) Fieser, L. F., J. Amer Chem. Soc., 76 1945 (1954).

(41) Fieser, L. F., J. Amer Chem Soc., 75 4386 (1953).

(42) Seeback, D., Jones, N. R., and Corey, E. J., J. Org. Chem.,33, 300 (1968).

(43) Handbook of Silylation, Pierce Chemical Company. P. O. Box 117, Rockford, Illinois 61105, 1972, pp. 19-20.

(44) Corey, E. J., J. Org. Chem.,32, 4160 (1967).

(45) Brown, R., Adv. Org. Chem., 3 89 (1963).

(46) Miller, D. F., Schwartz, W. E., Jones, P. W., Joseph, D. W., Spicer, C. W., Riggle, C. J., and Levy, A., "Haze Formation: Its Nature and Origin", second annual report of the U. S. Environmental Protection Agency and the Coordinating Research Council, submitted by Battelle, Columbus Laboratories, June 1973.

(47) Mayer, R., Bochow, K., and Zieger, W., Z. Chem.,4, 348 (1964).

(48) Jones, P. W., and Adelman, A. H., "A Novel Preparation of Cyclic Sulfites through Photosulfoxidation of Alkenes", Tetraheldron, 30, 2053, (1974).

(49) Cockcroft, R. D., Meali, E. E., and Rhodes, S. J. Tetrahed. Lett., 41, 3539 (1970).

(50) Simonsen, J. L., "The Terpenes", Vols. I and II, Cambridge University Press, London, c. 1953.

(51) Templeton, W., "An Introduction to the Chemistry of Terpenoids and Steroids", Butterworth and Company, Ltd., London, c. 1969.

(52) Simonsen, J. L., op. cit., Vol II, p. 140.

(53) Spencer, C. C., Weaver, W. I., Oberright, E. A., Sykes, H. J., Burney, A. L., and Elder, A. L., J. Org. Chem.,610, 5 (1940).

(54) Simonsen, J. L., op. cit. Vol. II, pp. 136-139.

(55) Templeton, W., op. cit. p. 62.

(56) Banthorpe, D. V., and Whittaker, D., Q. Rev. Chem Soc., 20, 373 (1966).

(57) Templeton, W. op. cit. pp 67-68.

(58) Simonsen, J. L., op. cit. Vol I, p. 300 and p. 166.

(59) Dupont, G., and Zacharowitz, W., and R. Deilou, Compt. Rend., 198, 1699 (1934).

(60) Henderson, G. G., and Sutherland, M. M., J. Chem. Soc., 101 2288 (1912).

(61) Gay, B. W., and Bufalini, "Hydrogen Peroxide in the Urban Atmosphere", paper presented at the 161st American Chemical Society National Meeting, Los Angeles, March 1971.

(62) Simonsen, J. L., op. cit., Vol II p. 141.